Potential Applications of Electrospun Nanofibers in Agriculture

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Abstract

Some of the major challenges associated with current agricultural practices include inefficient delivery and utilization of agrochemicals; fertilizers, pesticides, and pheromones; to crops. This results in low nutrient utilization efficiency with respect to applied fertilizers which leads to a greater economic burden to farmers to maintain crop yields at optimum levels. In addition, plant diseases by various pathogens also pose a threat to agriculture. In an effort to address some of the aforementioned challenges, electrospun nanofibers have emerged as a potential class of one-dimensional nanomaterials for use in agricultural applications. Unique characteristics of electrospun nanofibers such as enhanced surface area: volume ratio, high porosity distribution, and increased specific surface area pave the potential for agricultural applications that will be elaborated in this review. These applications include slow-release of fertilizers, pheromones and insecticides, seed and fruit coatings, plant protection, and nanofiber fabricated sensors. In addition, this review also focuses briefly on other preparation methods of nanofibers, and most importantly on the parameters that govern the electrospinning process; solution parameters, processing parameters, and ambient parameters. Furthermore, many more unexplored applications in the field of agriculture employing nanofiber usage exist, and it is believed that a greater understanding of the current nanofiber research and practices of green electrospinning will enable the upliftment of current boundaries to enable agricultural applications of nanofibers on a commercial scale.

Keywords: nanofiber - agriculture - electrospinning - slow-release – sensor

1. Introduction

Upon evaluation of current agricultural practices and data, it is evident that certain aspects of agriculture need to revolve more around the concept of agricultural sustainability to cater to the growing food demand while keeping the environmental risk at a minimum (Liu et al., 2006). It has been reported that the efficiency of pesticides and fertilizers has significantly decreased in a study conducted from 1961 to 1980 for cereal crops. This has been attributed to several reasons such as a decrease in plant sensitivity to the chemicals or even changes in conventional agricultural practices while evolutionary interactions between biotic components have also partly been responsible for a reduction in pesticide efficiency. The reduction in efficiency requires increased amounts of these chemicals to achieve the desired results.

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Liu and co-workers have depicted the problems associated with increased usage of fertilizers since the crops utilize just a fraction of the fertilizers added to it and the rest is a loss (Liu et al., 2010). This is termed low nitrogen utilization efficiency by plants. Nitrogen leaching can occur in several ways such as by water-soluble nitrates, ammonia, and nitrogen oxide emissions and incorporation into the organic matter of soil over time via processes mediated by microorganisms (Monreal et al., 1986). In fact, between 50- 70% of applied nitrogen is lost (Kottegoda et al., 2017). This leads to an extra cost to get nitrogen to the plant while also posing a major environmental risk both to biotic and abiotic components.

Mac Donald et al have reported the environmental risks associated with the leaching of fertilizers which include surface water eutrophication, reduction in downstream water quality, soil acidification, biodiversity loss and tropospheric ozone and smog (MacDonald et al., 2011). Heckel and co-workers have pointed out that pesticide resistance is a growing concern and will require higher doses of pesticide to control pests (Heckel, 2012). It has been reported that insecticide-resistant insects and herbicide-resistant weeds can evolve within a decade or two respectively. Duhan et al have mentioned that repetitive use of herbicides leads to plant damage, reduction in soil fertility, soil pollution, and weed resistance (Duhan et al., 2017).

By taking into account the aforementioned drawbacks in agricultural practices, this review presents potential agricultural applications with nanofiber usage that can minimize or prevent these drawbacks (Sun et al., 2012). Furthermore, the author also presents the advantages and challenges associated with nanofiber usage under each respective application.

2. Advantages of developing nanomaterials and nanofiber-based materials in agricultural applications

Nanofiber usage in agricultural applications is in a juvenile stage. However, its potential in this field ensures that as the understanding of nanotechnology increases, agricultural applications with nanofibers can be utilized to give maximum benefits (Ioannou et al., 2020). A nanomaterial, in general, is referred to as a material that is produced on the nano-scale; 1-100 nm with a specific property and composition (Kreyling et al., 2010). Herein, specific agricultural functions that can be carried out by nanomaterials i.e. nanofibers are explored. Nanofibers have interesting characteristics that have led them to be considered an important class of 1-D nanostructures (Persano et al., 2013). Nanofibers from electrospinning typically can have diameters as large as 500 nm and as low as 3 nm (Khan et al., 2013). Some characteristic features are high surface area, tailorable porosity distribution (Haider et al., 2014), versatile surface morphology and superior mechanical performance (Lasprilla-Botera et al., 2018). Advantages of nanofibers in agricultural applications include simplicity, high contact surface and high porosity distribution (Meraz-Dávila et al., 2021).

Nanomaterials allow for the slow-release of agrochemicals in reduced dosage (He et al., 2019). This results in better nutrient delivery to the plant and minimum loss to the environment (Solanki et al., 2015). Furthermore, it has been stated that nano-fertilizers contribute to the aforementioned enhanced nutrient delivery as a result of their high surface area to volume ratio, slow-release in response to environmental stimuli and their target delivery mechanisms.

Enhanced seed germination has also been reported with nanomaterials due to the penetration of nutrient-loaded nanomaterials into the seed. Literature has reported the potential of nanomaterial in the field of pest management once again due to factors such as slow-release and the need for a lower dosage than recommended (Duhan et al., 2017). Unwanted movements of pesticides and reductions in organic solvent runoffs can be achieved with nanopesticides due to better affinity to target pests as well as high surface area to volume ratio. Nanofungicides have also been reported to offer better plant protection due to their antibacterial and photocatalytic activity such as TiO_2 nanoparticles (Kutawa et al., 2021) The herbicidal activity of the active compound has been reported to increase upon nano-encapsulation (Oliveira et al., 2015). Nanosensors are another potential agricultural application that has been reported in the literature. The monitoring of soil and aquifer contaminations' (Prasad et al., 2017) and possible uses in the detection of plant pathogens and for crop health monitoring have also been reported(Chaudhry et al., 2018). The advantages of nanosensors that aid in the aforementioned uses include low detection limits, better sensitivity, convenient size, and reduced response time (Khot et al., 2012).

Electrospun nanofibers also possess certain limitations. It has been reported the variety and number of polymers that can be used to fabricate organic nanofibers are limited. In addition, certain inorganic nanofibers have limited performance and application range due to issues such as friability post calcination process. Furthermore, scaling up electrospinning at industrial levels to produce electrospun nanofibers are still more expensive than traditional methods of producing nanofibers (Shi et al., 2015).

2.1 Electrospinning technique

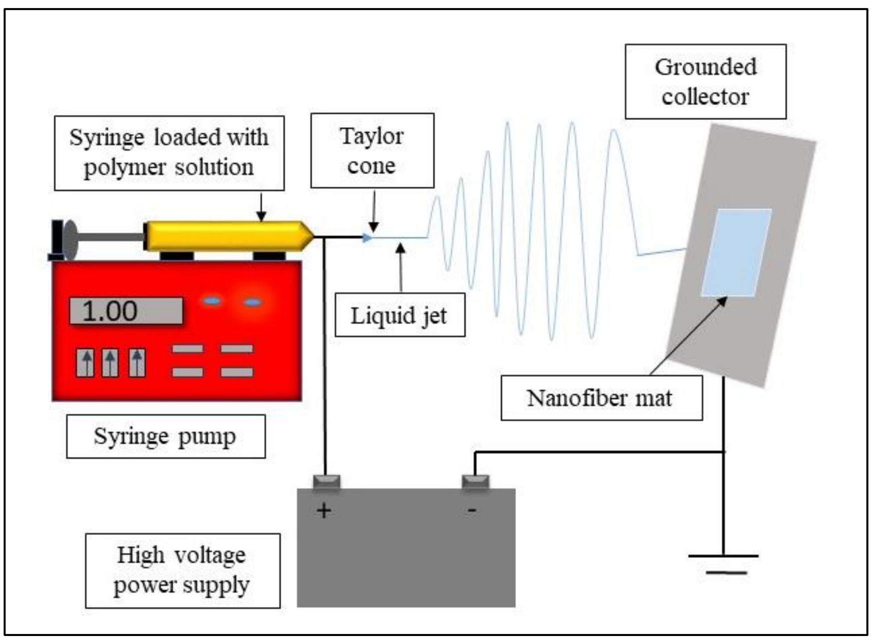

Figure 1. Typical electrospinning set-up

A typical electrospinning set-up includes a syringe pump, a spinneret/(s), a power supply of high voltage and a grounded collector. The set-up can be either vertical or horizontal. In this process, the liquid droplet that extrudes from the tip of the spinneret forms a pendant droplet due to surface tension. Upon

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application of high voltage to the tip of spinneret, the electrostatic repulsions due to similar surface charges establish. At the critical voltage, the electrostatic repulsions overcome the pendant droplet's surface tension causing it to undergo deformation to a Taylor cone that ejects a charged jet. Initially, the jet is drawn towards the grounded collector in a straight line which soon experiences a whipping motion owing to bending instabilities. The jet which consists of a charged polymer stream, while undergoing whipping motion, solidifies into finer nanofibers when its solvent evaporates and finally gets deposited on the grounded collector (Ibrahim and Klingner, 2020). The advantages of this technique over other conventional nanofiber formation techniques include cost-effectiveness, relative convenience of usage (Thavasi et al., 2008), and above all convenient incorporation of the active material of interest (Subbiah et al., 2005). Electrospinning not only produces solid nanofibers but can also be manipulated to form hollow, porous or core-sheath nanofibers (Xue et al., 2017).

2.2 Parameters of electrospinning

The parameters that affect the process of electrospinning can be broken into three categories. They are ambient parameters, solution parameters and processing parameters (Ibrahim et al., 2020) (Tirgar et al., 2018). Solution parameters are the following properties of the solution which include its surface tension, viscosity, type of solvent, concentration, conductivity, and molecular weight. Processing parameters are the voltage applied, flow rate, needle tip diameter, collecting electrode type and needle to collector distance. Surrounding temperature and humidity constitute the ambient parameters. The role of these parameters has been addressed greatly in literature and Table 1 presents a very brief summary in this regard. Appropriate parametrization is essential for the production of nanofibers without beads and desired morphology.

Table 1. Parameters of electrospinning and their effects on electrospinning

Parameter	Effect on electrospinning	Reference
Solution parameters		
1. Concentration	Electrospinning occurs at moderate polymer concentrations. At very high polymer concentrations, the high viscosity associated with the solution can cause clogging of the needle tip. Ex: Cellulose acetate of MW 100,000 Da electrospun only in the range of 9% to 15% (w/v).	Angel et al.,2019
2. Viscosity	At lower viscosities, beads are formed mostly. Very high viscosities make it difficult for the polymer solution to extrude from the spinneret tip and drying at the tip may also occur. Ex: 5% PVP with glacial acetic acid: titanium tetraisopoxide ratio less than 0.43 resulted in beaded nanofibers.	Sadeghi et al.,2018
3. Surface tension	Moderate surface tension is required. Can lead to the formation of beaded nanofibers with high surface tension.	Valizadeh et al., 2014

4. Conductivity	Too high a conductivity affects Taylor cone formation. Moderate conductivity promotes nanofibers with fewer beads. Ex. The addition of dimethylformamide (DMF) to polycaprolactone/dichloromethane solution increases conductivity and promotes lesser bead formation.	Du et al.,2016
5. Molecular weight	Too low a molecular weight will give rise to beads. Micro-ribbon formation occurs with too high a molecular weight.	Islam et al., 2019
6. Solvent type	Highly volatile solvents can be problematic. Solvent properties such as dielectric constant and polarity affect solution conductivity as well. Ex. Smooth nanofibers were produced with polyimide in DMF but ribbon formation occurred with polyimide in 1, 1, 1, 3, 3, 3-jexafluoro-2propanol.	Guo et al., 2022 Kohse et al., 2017
Processing parameters		
1. Applied voltage	High voltage leads to nanofibers of smaller diameters. Ex. Kerafin/PVA nanofibers were electrospun at 12, 15, 18, and 20 kV and with the increase of voltage, the recorded diameters were lesser.	Ziyadi et al., 2021
2. Flow rate	Flow rate determines electrospun nanofibers' diameter, porosity and geometry. A higher flow rate accounts for higher nanofiber diameter. Ex. Polyimide nanofibers electrospun at 0.25, 0.5, 1, and 2 mLh^{-1} showed increase in diameter with increase in flow rate.	Topuz et al., 2021
3. Collecting electrode	If the collector is made of a weak conducting material, less nanofibers and more beads will be formed.	Ibrahim et al., 2020
4. Distance from needle to tip	With the increase of distance from needle tip to collector, the fiber diameter decreases. Shorter distances have reported the formation of beaded nanofibers.	Ibrahim et al.,2020
5. Diameter of needle tip	With reduction in the internal needle diameter, clogging of the polymer solution can take place. Furthermore, it can lead to nanofibers with a smaller diameter. Ex.	He et al., 2019

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	PEO nanofibers electrospun at needle diameters ranging from 0.51 mm (nanofiber diameter of 170.5 ± 28.0 nm) to 1.32 mm (194.2 ± 54.7 nm) showed the aforementioned pattern.	
Ambient parameters		
1. Temperature	Lower evaporation of solvent has been recorded for lower temperatures and thus longer time required for polymer jet solidification. . A moderate increase in temperature can promote nanofiber without bead formation. Ex. Chitosan nanofibers electrospun at 20°C, 22°C, 27°C, and 32°C exhibited remarkable change from bead formation to smooth nanofibers with increase in temperature.	Van-Pham et al., 2020
2. Humidity	Affects the rate of evaporation of solvent from the charged jet. This in turn will affect the fiber diameter.	Mailey et al.,2020

3. Potential applications of electrospun nanofibers in agriculture and their advantages and challenges

3.1 Slow-release fertilizers (SRFs)

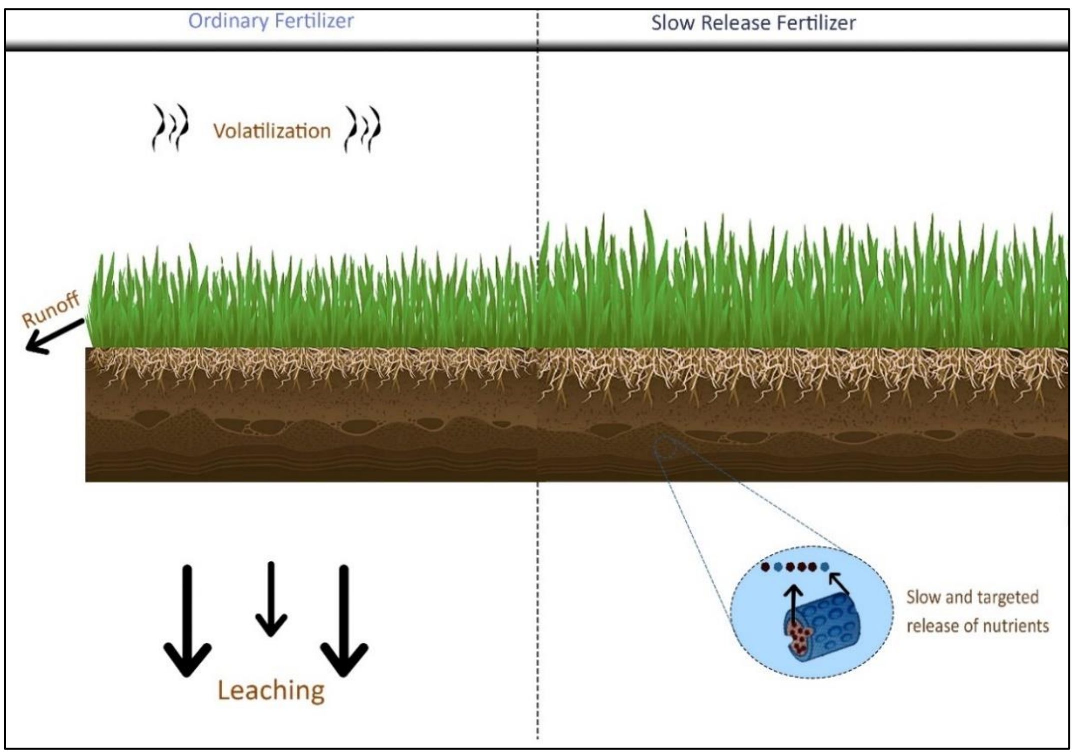

Figure 2. Advantages of SRF in comparison to an ordinary fertilizer

As given in Figure 2, it is well accounted for in the literature that slow-release fertilizers exhibit advantages with respect to ordinary fertilizers. The latter cannot promote a sustained slow release of nutrients leading to various environmental issues such as volatilization of ammonia, leaching, and runoff (Wei et al., 2020). A SRF is a type of value-added fertilizer that consists of a plant nutrient/(s) where its availability is delayed or extended to the plant (Fu et al., 2018). Due to its many advantages such as increase of nitrogen uptake efficiency by reduction of nitrogen losses via processes such as leaching, volatilization and runoffs, SRFs have become pioneers of modern agriculture.

Table 2. Examples of electrospun nanofibers investigated as potential slow-release fertilizers

Research Group	Electrospun nanofibers as slow-release fertilizers	Highlights in slow-release
Enriquez et al.,2012	8% w/v wheat gluten nanofiber mat	The urea release kinetic studies showed to have a burst release during the first 10 minutes releasing 56% of the total urea. Equilibrium was attained in 300 h after a gradual decline in the release rate of urea, releasing a total of 98% of urea.
Hassounah et al.,2014	Polyvinyl alcohol (PVA) and polyethylene oxide (PEO) polymer matrices. Loaded separately with 0%, 10% and 20% and 0%, 20% and 25% of urea respectively.	Due to their pore distribution, it allows for the mats to capture water
Azarian et al., 2018	A 19.5 w/v PVA containing 3% montmorillonite (MMT) and MMT-urea separately.	Slow-release studies not done
Nooeaid et al.,2021	Nitrogen, phosphorus and potassium (NPK) loaded co-axial nanofibers as well as PVA uniaxial nanofibers. The core of the nanofiber was fabricated with PVA while polylactic acid (PLA) was used for its shell fabrication.	Subjected to plant development and growth assessments with green and red cos lettuce which showed promising results. However, for height of plants, leaf count and dry weight, the tested SRF showed only closer results to the neat NPK usage.
Kampeerapappun et al.,2013	Co-axial nanofibers with polyhydroxybutyrate (PHB) for shell fabrication and PLA mixed with fertilizer for the core.	Electrospun nanofiber mat can release fertilizer for a time duration of 1 month without degradation. The nanofiber mat demonstrated to have a higher cumulative fertilizer release with an increase in core solution flow rate.

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3.2 As seed coatings

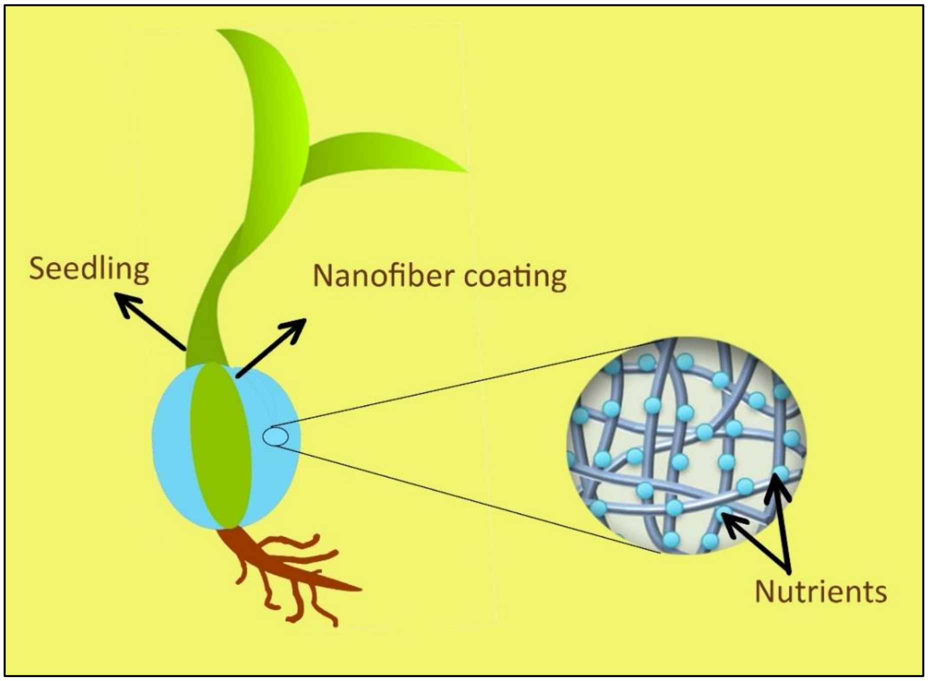

Figure 3. Electrospun nanofibers as a seed coating

Electrospun nanofiber mats for seed coatings as crop protection are also emerging potential agricultural applications. Cellulose diacetate nanofibers loaded with pesticides of abamectin or fluopyram were coated onto seeds. They demonstrated a slow and controlled release for the respective pesticide over a period of two weeks (Farias et al., 2019). Furthermore, it was also shown that the coating of the seed directly at the collector of electrospinning and the thickness of the coating did not have any negative effect on germination. Interestingly, fluopyram-loaded nanofibers also showed very positive results in the fungal assay against *Alternaria lineariae* which consistently showed greater inhibition zones than the positive control used.

Polyvinylpyrrolidone (PVP) was used to fabricate nanofibers loaded with urea as the source of nitrogen along with a micronutrient of cobalt nanoparticles for usage as cowpea seed coatings. However, due to the hydrophilic nature of PVP, an initial burst release was reported (Krishnamoorthy et al., 2016). In an attempt to overcome the aforementioned issue, the same group also electrospun nanofibers from a PVP and poly(diethoxy)phosphazene (PPZ) polymer blend. This, however, did not seem economical due to the increased cost of PPZ (Krishnamoorthy et al., 2018).

To improve the microbial inoculants at the interface of root-soil interface, nanofiber mats of a polymer blend of PVA/PVP with glycerol as a plasticizer were loaded with *Bacillus subtilis* plus *Seratia marcescens* (plant growth-promoting bacteria). They were coated onto seeds of *Brassica napus* L. (Hussain et al., 2019). It was reported that the rhizosphere of electrospun nanofiber-coated seeds had a denser population of growth-promoting bacteria than that of uncoated seeds and composite-coated seeds. However, the authors have recommended the use of this seed coating within 15 days from its manufacture date to get optimum results due to the reduction in the effectiveness of the coating with time.

Improving mycorrhizal inoculation in the rhizosphere has also been addressed by the use of nanofiber seed coatings. PEO nanofibers were used to release arbuscular mycorrhizal fungi in a slow and sustained manner to bean seeds (*Phaseolus vulgaris* L var. Jose Beta). The coated seeds showed a great increase in the flower bud count; an increment of 200% in comparison to the non-inoculated bean seeds as well as in both fresh and dry weight which increased approximately by 140 and 143% respectively(Campaña and Arias, 2020).

To address crop productivity in pathogen-infested soils, nanofiber coatings for seeds have been tested. In fact, nanofiber seed coatings that release copper has been reported to improve seed germination in pathogen-infested soils that resulted in an increment of 12-29% improvement in the biomass of seedlings given the other growth conditions are optimum (Xu et al., 2020). Also, in healthy conditions, the biomass seedling of both the tomato and lettuce has been shown to increase by the range of 12-29% in nanofiber-coated seedlings.

3.3 Slow-release of pheromones and insecticides

Pheromones are chemical substances targeted toward insects of the same species via triggering a behavioural response (Kikionis et al., 2017). The pheromone usage for plant protection has been employed with various techniques such as spraying if the pheromone incorporated medium is a fluid or mechanical distribution/ evaporation if solid particles incorporate them. However, such methods are susceptible to strong winds and rains requiring periodic applications and increased costs. Hence, slow-release by electrospun nanofiber mats offer an effective distribution profile of pheromones (Hellmann et al., 2011).

Kikionis et al have developed separate slow-release pheromone-loaded nanofiber mats containing (Z)-7-tetradecenal (7Z14ALD) against *Prays oleae Bern* and 1, 7-dioxaspiro [5.5] undecane (DSU) against *Bactrocera oleae Rossi*. (Kikionis et al., 2017) The pheromone loadings were reported as 5%, 10%, and 20% w/w in cellulose acetate (CA), polycaprolactone (PCL), and PHB. The controlled release of 7Z14ALD was reported for nearly 16 weeks with both CA and PCL as opposed to DSU-loaded CA/ PHB which exhibited fast release within the first two weeks. Laboratory bioassays for 7Z14ALD mats showed better insect response than the positive control in just the 5% w/w pheromone loading category but not for the other loadings. Field trials of *P.oleae* showed results lower than the positive control except for PCL-7Z14ALD-5% w/w which exhibited almost three times the attractiveness than a positive control in the first flight period considered. The positive control employed was simply a DSU-impregnated filter paper.

Hellmann et al have fabricated 20wt% polyamide 6 (PA 6) nanofibers and 10% wt CA with loadings of the pheromone (Z)-9-dodedecenyl acetate up to 20 wt% of pheromone and loadings from 20 to 33.3 wt% respectively (Hellmann et al., 2011). The author highlighted a phase separation and elongation of the loaded pheromone in the PA 6 nanofibers, with dispersed pheromone region diameters of 20-30 nm and length of dispersion of 100-150 nm. On the other hand, the authors observed no pheromone 'islands' with the CA nanofibers that suggested no phase separation of the pheromone with the CA nanofibers unlike in PA 6 nanofibers. On closer inspection, coarsening in CA nanofibers was observed which was attributed to nanoscale concentration fluctuations. In vitro studies of the pheromone release demonstrated approximately linear kinetics and even after 55 days of release studies, the CA nanofiber mats exhibited a significant amount of pheromone. This gives it the potential to be applied for the protection of longer lifespan plants as well.

Jorge and co-workers developed nanofibers from a blend of PCL and polyethylene glycol polymers to contain both a pheromone and an insecticide (Czarnobai De Jorge et al., 2017). The sex pheromone of *Grapholita molesta* (Lepidoptera: Tortricidae) (Busck) and cypermethrin (an insecticide) loaded together and separate were tested using mortality bioassays and male electroantennographic responses. The authors

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have found that the nanofibers loaded with only pheromone and pheromone plus insecticide both showed equivalent EAG responses. This proved that the insecticide did not interfere with the attractiveness of the pheromone and can be used effectively in the same nanofiber mat. It was also shown via the tarsal-contact mortality bioassay that the insecticide can provide prolonged insecticidal activity since it is capable of giving an 87.5% mortality rate even after prolonged exposure of 84 days to the nanofiber mat. Furthermore, the main advantage of the use of nanofibers in this context is to reduce or avoid the burst release of the active ingredients from the nanofiber mat.

Xiang et al demonstrated the use of an electrospun nanofiber mat of PLA incorporated with cellulose nanocrystals for the slow release of thiomethoxan (Xiang et al., 2013). Initial studies were done using a model insecticide drug known as Columbia Blue because it exhibited similar properties to that of a real pesticide in terms of its molecular weight and its octanol/water partition coefficient. Results showed that for hydrophobic insecticides, the increase of the percentage of the cellulose nanocrystals incorporated resulted in a faster release while polymer degradation mechanisms and diffusion were also contributing factors. The greenhouse trials of this study were done using an actual insecticide; thiomethoxan. The authors concluded that, even at 50% of the recommended dosage of the insecticide, the nanofiber mats were effective in a 9-day greenhouse trial that was conducted. With an increase of the loading percentage of the insecticide, the percent mortality increased. However, 100% percent mortality was reached with a nanofiber loading of 200% of the recommended dosage which is not viable economically.

Integrated pest management strategy is also an important field sought after in agriculture (Mahdavi et al., 2017) which also includes the development of biopesticides. Studies have shown the use of pure essential oils (PEO) as an alternative biopesticide. However, their rapid degradation and high cost of production limit their usage for this purpose. Mahdavi et al have demonstrated that the use of nanofibers for entrapment of PEO can overcome the aforementioned limitations while also contributing to an effective insecticidal activity. In this study, the authors have fabricated 10% w/v PVA nanofiber mats and PEO with cinnamaldehyde as the active ingredient. Fumigant toxicity studies showed a statistically significant difference in the insecticidal activity when PEO was applied as it and as a nanofiber oil (NFO) with the NFO showing greater results. Furthermore, the residual effect of NFOs was more than 40 days while that of the PEO was just 15 days. It has led to the conclusion that the nanofiber mat can protect the PEO against degradation.

Allahvaisi et al have also reported the effectiveness of PEO loaded onto nanofiber mats. (Allahvaisi et al., 2017) Essential oils from *Mentha piperita L*. and *Salvia officinalis L*. were loaded up to 22 wt% in the matrix of PLA polymer. The NFOs showed release of essential oil and mortality rates even after 40 days of exposure whereas the PEO lost its insecticidal activity just after about 14 days which will require reapplication and thereby lead to increased economic burdens.

3.4 Sensors

One of the main advantages of an electrospun membrane as a chemo sensor is that they have a lower limit of detection (LOD) such as the cross-linked electrospun curcumin-loaded nanobelt-shaped zein membrane that has a LOD of 0.3 mg/L (Qiao et al., 2019). This is primarily due to the high surface area to volume ratio of the electrospun membrane that they can incorporate more chemosensors. However, in comparison to other nanomaterials used as sensors, electrospun membranes are reported to have zero transducer ability so such membranes can only be used as receptor substrates in the sensor but not as a transducer (Zhang et al., 2017). Furthermore, the low cost for fabrication of an electrospun membrane, its high porosity density, convenient fabrication, almost no pollution effects to detection solution and above all easy post-treatment methods after usage of the sensor make them appealing to be used as chemosensors. Features such as durability (Yu et al., 2016) and elastic ability are also seen in flexible sensors designed with electrospinning. Flexible sensors are important in agriculture since they afford the rapid production of small batches of sensors (Huang et al., 2023).

It has also been reported that nanofibrous membranes from electrospinning have been used for the fabrication of optical chemosensors (Zhang et al., 2017) which adds to the advantages such as convenient observation even by the naked eye, reduced costs and potential for massive production.

On the other hand, it has to also be stated that certain challenges govern the use of a nanofiber mat as a biosensor. It is mainly attributed to the control of some characteristics such as the hydrophobicity/ hydrophilicity nature of the polymer and the relevant specific surface functionality for sensor application. If the polymer is hydrophobic, it will hinder sensor performance in aqueous systems while if the polymer is hydrophilic it will degrade too soon in aqueous systems. In this review, sensory applications for heavy metal detection and pesticides will be discussed briefly.

3.4.1. Sensors- heavy metal detection

Heavy metal ions can be detected with nanofiber fabricated sensors. One such frequent application is the detection of mercury ions via aptasensors involving the binding of Hg^{2+} with thymine bases. The nanofibers in some sensors aid in the amplification of signals generated by the presence of the mercury ions given by the binding of Hg^{2+} ions with thymine bases of DNA and methylene blue (Ehzari et al., 2019). These sensors also showed sensitivity, stability and reliability in both the test and real samples (Teodoro et al., 2019) (Xie et al., 2021). Besides the Hg^{2+} ions, other reported detections include those of Cd^{2+} (Liu et al., 2020), Pb^{2+} (Oliveira et al., 2020), As^{3+} (Tang et al., 2020), Fe^{3+} (Zhang et al., 2019) and Cu^{2+} which also showed aforementioned properties. It has to be pointed out that some sensors could detect more than just one metal ion such as a colorimetric sensor based on a hydrogel membrane fabricated from poly(aspartic acid) electrospun nanofiber which detected both Fe^{3+} and Cu^{2+}. It is also a reusable sensor.

Electrospun zein nanomembranes loaded with curcumin, in heated and unheated forms, were tested for detection of Fe^{3+} and Fe^{2+} and found to have LOD of 0.3 and 1 mg/L respectively (Qiao et al., 2019). Upon incubation in a 10 mg/L Fe^{3+} at a pH of 2, the heated membrane showed a color change from yellow to dark brown while the unheated membrane showed a color change from dark yellow to brown. Interestingly, the unheated membrane exhibited a better visual change in terms of its color due to a higher surface area than that of the heated membrane which had cross-links formed during its heating and hence a width reduction.

3.4.2 Sensors- pesticide detection

One common mechanism employed by biosensors for pesticide detection includes the immobilization of the acetylcholine esterase (AChE) (Moradzadegan et al., 2010). While many methods for the enzyme immobilization have been reported such as via covalent bonds and physical adsorption onto a solid support, electrospun nanofibers have been investigated as better encapsulating media for AChE. The high surface area of the nanofiber mat provides a better rate of enzyme loading per unit weight of the mat in addition to increasing the catalytic effectiveness of the enzyme (Stoilova et al., 2010). Furthermore, immobilization of enzymes in nanofiber mats allows for the re-use of the enzyme and stability over high pH and temperatures which otherwise would not have been possible.

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Moradzadegan et al have successfully immobilized an AChE and Bovine Serum Albumin mixture in 6% w/w PVA matrix (Moradzadegan et al., 2010). It was reported to have a maximum recovery of activity at 40% after immobilization. It was also reported to have an initial activity of 70% after ten consecutive uses. However, the authors state that some percentage of the enzyme may not be chemically bound but physically resulting in their loss. Furthermore, the hydrophilicity of PVA results in fiber enlargement and enzyme loss.

Stoilova et al have developed electrospun nanofiber mats from styrene–maleic anhydride copolymers at 1:4 w/w and 1:1 w/w and functionalized with spacers i.e. Jeffamine and p-phenyl enediamine to immobilize AChE (Stoilova et al., 2010). They found that the AChE immobilized Jeffamine modified nanofiber mat exhibits increased specific activity as that of the free AChE. It was reported that AChE immobilized mat's thermal stability was considerably maintained for a longer time period in comparison to the free enzyme. Furthermore, the nanofiber mat's storage stability was better than the free enzyme with more than 30% of activity retention whereas the free enzyme had only 19%. The operational stability was also good where the authors had reported a 65% loss of activity after 10 reusable cycles.

Supraja et al fabricated a biosensor of electrochemical type for the trace detection of atrazine (1-chloro-3-ethylamino-5-isopropylamino-s-triazine) with multi-walled carbon nanotube – zinc oxide based nanofiber 68. The study reports the sensitivity of the sensor as 21.61 (KΩ μg^{-1} mL^{-1}) cm^{-2} and LOD as 5.368 zM (Supraja et al., 2020).

3.5 Fruit coatings

The use of electrospun nanofibers as fruit coatings in comparison to traditional film coatings includes the following benefits: allowing for facile encapsulation of active ingredients, better nanoporosity, and undoubtedly an enhanced surface area: volume ratio (Kurtz and Schiffman, 2018). Literature reports that polyacrylonitrile electrospun nanofibers deposited with TiO_2 nanoparticles (PAN@TiO_2) serve as effective packaging films that scavenge ethylene. For example, tomato fruits coated with PAN@TiO_2 electrospun nanofibers produced more than 50% lower levels of ethylene post 2 weeks of storage with respect to the control tomato fruits which produced close to 1 µmol $kg^{-1}h^{-1}$ ethylene. In addition, the firmness of the nanofiber-coated fruits was recorded to be higher (150 N/cm^2) in comparison to the control (100 N/cm^2) after 2 weeks of storage time (Zhu et al., 2019). Cherry rain cracking is disastrous to economic cherry cultivation since it involves the bursting of the cherry skin due to an increase of osmotic potential within the fruit. Approximately 55% rain cracking has been reported in the Pacific Northwest in 2005(Long et al., 2005).

Jung et al have fabricated cellulose nanofiber of 0.5% w/w along with potassium sorbate of 0.5% w/w and various plasticizers i.e. glycerol, sorbitol, and PEG-400 along with a surfactant mixture of Tween 80 and Span 80 (1:1 ratio) at 0.05%, 0.1%, and 0.2% concentrations. (Jung et al., 2016) Lab-scale optimization trials reported 0.1% glycerol usage for an effective coating. Hence the three formulations 0.5% cellulose nanofiber, 0.1% glycerol, and 0.5% potassium sorbate, with 0.05%, 0.1%, and 0.2% surfactant concentrations were employed in field trials in Coihueco and Angol as summarized in Table .3 which depicts the percentage reduction in cracking with variations in surfactant percentage.

Table 3: Percentage reduction in cherry cracking due to nanofiber formulations

Field trial location	Surfactant % in nanofiber mat	% reduction in cherry cracking
Coihueco	0.05	Not reported
	0.1	39.20

	0.2	31.18
Angol	0.05	68.07
	0.1	91.60
	0.2	55.70

Furthermore, the authors have mentioned that there is no effect of the nanofiber coating on the growth of the cherries. However, phytotoxicity studies on this coating formulation were not reported and there were no reported visual changes observed on the cherry fruit.

The use of nanofiber mats in fresh fruit keeping has also been reported. The porosity distribution in the nanofiber mat allows for the breathability of the fruit to an appropriate level thus providing a good environment to the fruit (Exama et al., 1993).

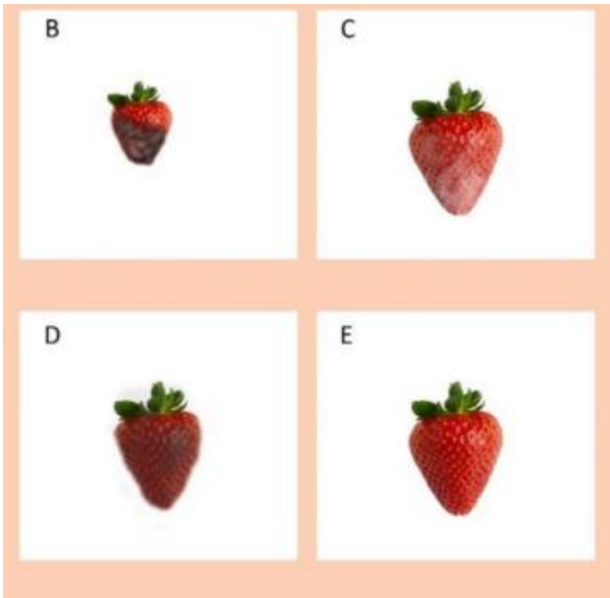

Figure 4. Four treatment groups in the determination of the effectiveness of nanofiber coating for strawberries: B) complete exposure to atmosphere C) wrapped with polyethylene D) coating of PEO: CMCS, 1:20 (electrospinning solution) E) coated with electrospun nanofibers.

Yue and coworkers developed carboxymethyl chitosan (CMCS)/PEO nanofiber mats as post-harvest coatings of strawberries. As depicted in Figure 4, all other treatment groups (B-D) were infected with rot and fungus except for the strawberries filmed with the CMCS/PEO electrospun nanofiber mats which the authors have concluded to be used as an effective tool for fresh fruit-keeping.

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3.6 Protection against plant diseases

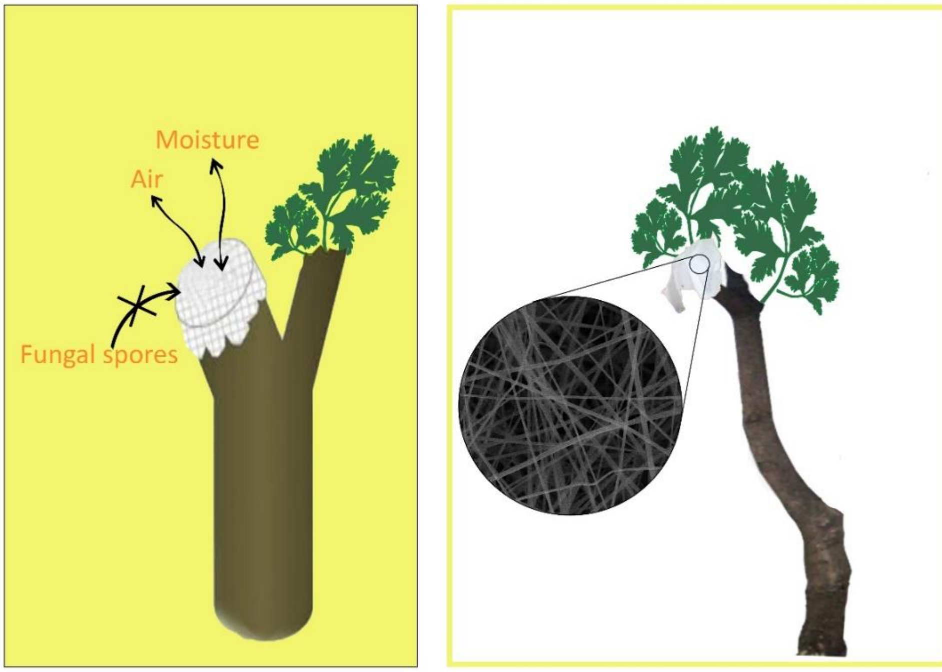

Figure 5. Nanofiber mat to cover the pruning wound of a plant

Buchholz et al have fabricated a non-woven nanofiber mat with a polymer blend of poly(butylene adipate-co-terephthalate) (PBAT) and an antimicrobial polymer of polyhexamethylene guanidine (PHMG) and also from polymers of polylactide/glycolide copolymer (PLGA) and PBAT (Buchholz et al., 2016). This was fabricated as an effective means to control the Esca disease on vineyards as a result of infection by the fungal spores of *Phaeomoniella chlamydospora* mode of action was to cover the pruning wounds of vines, which are the primary entry points to the spores, with the anti-fungal nanofiber mat while allowing for the exchange of gases and water to the plant. It was reported that the PLGA/PBAT nanofiber mat did not have 100% barrier efficiency against the spores yet the highest thickness analyzed (221 μm) showed an efficiency of 99%. However, spore colony formation on the nanofiber mat surface was reported in this case. On the other hand, PBAT/ PHMG nanofiber blend that has antifungal activity showed 100% efficiency as a barrier and no spore colonization on its surface was reported. Hence the authors have suggested this strategy as an effective tool for the prevention of Esca disease via pruning wounds.

4. Preparation of nanofibers

A variety of raw materials have been reported for use in nanofiber fabrication including natural and synthetic polymers, composite nanomaterials, carbon-based nanomaterials and semiconducting nanomaterials (Lim, 2017). A nanofiber is defined as a fiber fabricated to nano-scale in terms of its diameter (Liu.1997). This section entails several other approaches that exist for nanofiber fabrication besides electrospinning.

Self-assembly in solution is used to prepare nanofibers with smaller diameters. This is done by the formation of nanoscale supramolecular structures via assembling of individual molecules (Lim, 2017). The formation of chitin nanofibers from squid pen β -chitin solution in nanofiber ink of chitin has also been carried out (Hassanzadeh et al., 2013). Melt spinning produces fibers with diameters greater than 2 μm and involves the extruded strands of melted polymer (of a viscoelastic material) being drawn down to gradually reduce the fiber diameter (Ellison et al., 2007). Solution blow spinning is an integration of both the melt spinning technique and electrospinning. In this technique, the polymer solution is pumped through the inner nozzle via a syringe pump to a collector while the outer nozzle is filled with a high velocity gas at constant speed (Medeiros et al., 2009). CO_2 laser supersonic drawing is used to prepare long nanofibers without chemical solvent usage (Suzuki et al., 2014). Fibers with diameters in micro-range are melted by the laser and nanofibers are drawn from them via a supersonic airflow. Suzuki et al have reported the successful fabrication of nylon 66 nanofibers from this technique. In the jet blowing technique, hot, high-pressure gases such as argon or nitrogen are used to facilitate long nanofiber formation (Borkar et al., 2006). Some other techniques reported include template synthesis (Tao and Desai, 2007), phase separation (Zhao et al., 2011) and fibrillation (Sánchez et al., 2016).

5. Future Remarks

The use of nanofibers despite exhibiting great potential in agricultural applications has yet to develop in certain areas. One main concern is the use of non-biodegradable polymers and toxic solvents and the need to replace them with green electrospinning techniques. Furthermore, agricultural applications require the slow release of active ingredients for longer periods which will need further emphasis such as by use of co-axial electrospinning techniques for better encapsulation. The effect of nanofiber-loaded metabolites on plant metabolism has yet to be investigated and further phytotoxicity studies on nanofiber usage will need to be conducted although current studies have not reported any visual toxicity effects.

Nanofibers are employed to effectively eliminate contaminants in groundwater and surface water sources such as minerals, pathogens including viruses, fungi, bacteria, salts, cations, and other various types of monovalent and multivalent ions. This is due to the narrow distribution of pore sizes and high porosity (Mohammad et al., 2015). Nanofiber mats are effectively functionalized with various nanoparticles to aid in water purification such as the use of electrospun nanofibers with graphene oxide sheets coated removed salt at rates over 99.9% in membrane distillation (Li et al., 2020).

Besides the mentioned applications in this review, nanofibers can also be investigated on the ability to be used in advanced plant protection and reinforcement right from the time of germination by making use of the self-repair ability of polymer materials (Alemdar and Sain, 2008). Since certain nanofibers also aid in water retention, slow-release of water along with the agrochemicals can also be further investigated since they would serve as a great application in agriculture (Sekhon, 2014).

6. Conclusion

This mini-review provides an overview of the potential agricultural applications of nanofiber usage and the nanofiber advancements that offer the potential for them to be employed on a large scale basis in agricultural applications. The foregoing highlights the advantages of nanofibers over the conventional techniques used for certain applications in agriculture. It further emphasizes the fact that the application of nanofibers in agriculture is still in its infancy and hence presents scope for further research and development in understanding the process of nanofiber fabrication and application. More field studies will be required post-lab optimization to understand the cost-effectiveness and extent of practicality when it

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comes to large scale implementation of nanofiber usage. Moreover, a deeper understanding of the parameters governing nanofiber fabrication is essential to cater to different agricultural requirements.

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