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Metal–phenolic network-based edible coatings: a new class of antimicrobial and antioxidant barriers for fresh produce preservation

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Microbial growth, oxidative reactions, and moisture loss cause fresh fruits and vegetables (F&V) to quickly deteriorate after harvest, reducing their shelf life and market value. Although many current solutions rely on synthetic additives or offer poor functional endurance, edible coatings have been extensively investigated to inhibit these processes. An alternative method is provided by metal–phenolic networks (MPNs), which combine naturally occurring phenolic chemicals like gallic and tannic acids with food-grade metal ions like calcium, zinc, or iron. These ingredients work together to create thin, sticky coatings that are suitable for direct contact with fresh produce and have built-in antibacterial and antioxidant properties. Microbial cell membrane rupture, reactive oxygen species scavenging, and a decrease in oxygen and light exposure at the produce surface are just a few of the ways that MPN-based coatings work. Research on berries, oranges, apples, leafy greens, tomatoes, and other F&V shows reduced microbial counts, delayed browning, and better firmness and visual quality retention during storage. Uniform covering and compatibility with current post-harvest handling procedures are made possible by practical coating techniques, such as dip and spray application. Despite these benefits, there are still problems with large-scale processing, regulatory approval, metal ion dosage, and sensory perception. MPN coatings may be able to satisfy commercial needs while promoting safer and more sustainable fresh food preservation with further research into composition management and hybrid formulations.

Sustainability spotlight

Metal–phenolic network (MPN)-based edible coatings represent a sustainable alternative to conventional synthetic preservatives and packaging materials for fresh produce preservation. By combining naturally derived phenolic compounds with food-compatible metal ions, MPN coatings enable multifunctional protection properties like antimicrobial, antioxidant, and gas-barrier performance while reducing reliance on petroleum-based plastics and chemical additives. This review highlights green fabrication strategies, low-energy processing routes, and the potential integration of agricultural by-products as phenolic sources, aligning MPN edible coatings with circular bioeconomy principles. The adoption of such bio-inspired, biodegradable coating systems offers a promising pathway to reduce postharvest food losses and environmental impacts across the food supply chain.

1. Introduction

Postharvest deterioration of fresh fruits and vegetables (F&V) poses a significant threat to global food systems, increasing environmental burdens, reducing food supply, and causing financial losses.[1] After harvest, fresh produce remains physiologically active through transpiration, respiration, and enzymatic processes that accelerate the senescence process.[2] Simultaneously, oxidative reactions and microbial contamination cause spoilage, quality deterioration, and safety issues. Even under refrigeration, these factors cumulatively shorten shelf life throughout distribution, transportation, and storage.[3] There is a growing need for preservation techniques that are both efficient and compliant with clean-label requirements as consumer demand shifts toward fresh, minimally processed foods with fewer chemical ingredients.[4,5]

Edible coatings have attracted considerable interest as an alternative or complementary approach to conventional post-harvest treatments (Fig. 1). They serve as semi-permeable

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barriers that regulate gas exchange, minimize moisture loss, and limit metabolic activity.[6,7] Common coating materials include polysaccharides,[8] proteins,[9,10] and lipids,[11,12] such as chitosan, alginate, starch, cellulose derivatives, and natural waxes. Although these materials are typically regarded as safe and biodegradable, their functional effectiveness is often limited.[13] Many biopolymer coatings exhibit weak antibacterial and antioxidant activity, inadequate mechanical stability, or poor resistance to humidity.[14] As a result, their ability to reliably extend shelf life across diverse products remains limited. Active substances such as essential oils, organic acids, or plant extracts have been incorporated into biopolymer matrices to enhance the functionality of edible coatings.[15,16]

While this approach can improve antimicrobial or antioxidant performance, it also introduces challenges related to volatility, instability, sensory impact, and uncontrolled release. Also, the effectiveness of these additives may decline over time, reducing long-term protection. These limitations emphasize the need for alternative coating systems that balance structural integrity with intrinsic bioactivity while meeting food safety and legal requirements. Recently, metal–phenolic networks (MPNs) have emerged as a potentially useful material platform for the preservation of fresh fruit. MPNs are supramolecular structures formed when phenolic ligands coordinate with metal ions. Polyphenols, known for their antioxidant, antibacterial, and metal-chelating qualities, are abundant in nature and frequently ingested by humans.[17,18] Under mild, aqueous conditions, phenolic compounds can self-assemble into cross-linked networks when coordinated with metal ions such as iron, zinc, copper, or calcium. MPNs have been extensively investigated in various domains, including surface engineering, drug delivery, and environmental clean-up, due to their straightforward and adaptable fabrication method.[19]

MPN-based edible coatings differ from traditional edible coatings as they provide intrinsic functional activity in addition to their structural role. By scavenging free radicals and preventing oxidative processes that cause discolouration, nutritional loss, and textural degradation, phenolic ligands enhance antioxidant capacity.[20] By rupturing microbial membranes, interfering with metabolic pathways, or causing localised stress reactions in bacteria, metal ions can further increase antimicrobial potency, depending on their identity and coordination environment.[21,22] When metal ions and phenolics work together in a coordinated network, they often produce synergistic antibacterial and antioxidant effects that reduce the need for external chemicals.[23,24] The ability of MPN-based coatings to prevent light-induced deterioration is another noteworthy benefit. UV light can hasten oxidative damage and pigment degradation in fresh produce during storage and retail display because it is absorbed by several phenolic chemicals. MPN coatings may help retain colour, nutritional value, and overall attractiveness by serving as UV-blocking layers.[25,26] However, their semi-permeable nature permits enough gas exchange to avoid anaerobic situations, which can otherwise result in physiological illnesses and off-flavours.[27]

The development of edible MPN coatings is influenced by safety and regulatory concerns. Pure MPNs frequently have limited functionality, poor stability, and limited mechanical strength. To solve these problems, biopolymers such as proteins and polysaccharides are added to MPNs to offer properties such as improved mechanical strength, thermal stability, superior barrier qualities, and antioxidant and antibacterial properties. This will combine the functional benefits of metal–phenolic coordination with the film-forming capabilities of proteins or polysaccharides.[28,29] The practical application of MPN coatings has been further encouraged by advancements in fabrication

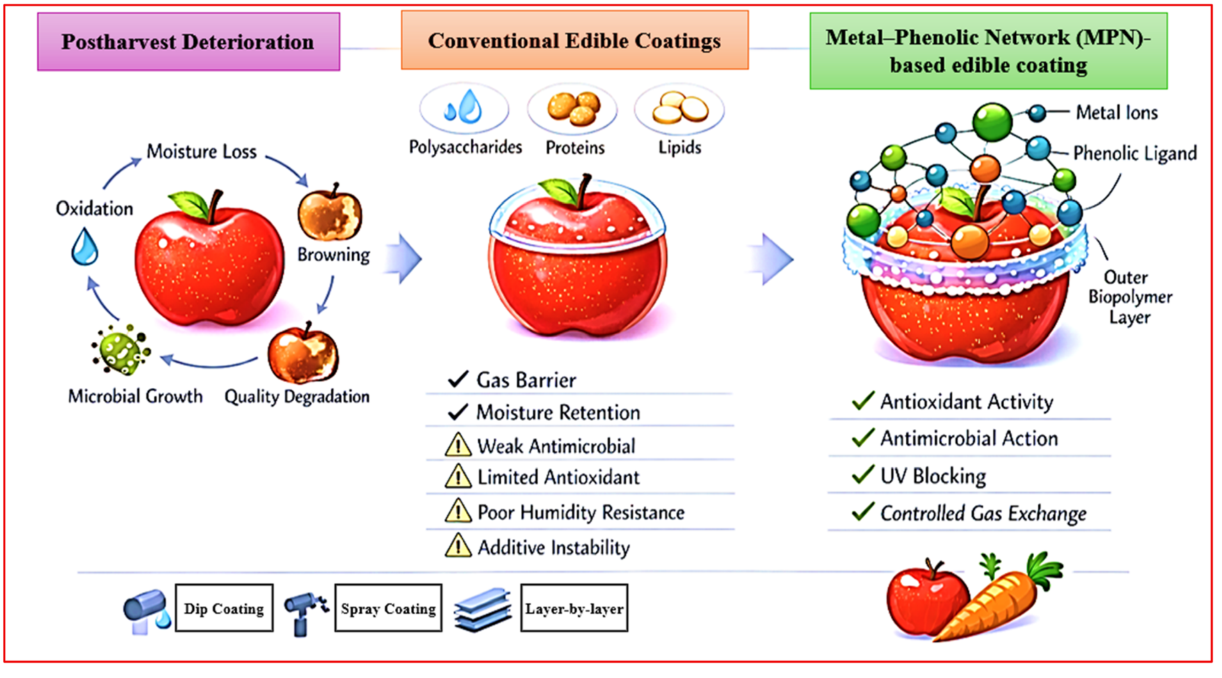

Fig. 1 Postharvest deterioration of fresh produce: limitations of conventional edible coatings and emerging MPN-based strategies.

techniques. Furthermore, controlled MPN film deposition on product surfaces is made possible by methods like dip-coating, spray-coating, and layer-by-layer assembly.[30] These techniques have the ability to be scaled up and are consistent with current postharvest processing processes. Despite obvious potential, the use of metal–phenolic networks (MPNs) in fresh food preservation is still in its infancy. Achieving sustained performance in commercial storage settings, guaranteeing sensory neutrality, and optimising coating formulations for various F&V are important issues. A deeper understanding of MPN chemistry, structure–function relationships, and interactions with plant tissues is necessary to address these problems. This review summarises the fundamental principles of MPN formation, their functional mechanisms, fabrication strategies, and reported applications in F&V. Current challenges and future opportunities are also discussed to guide further research and development in this evolving area.

2. Fundamentals of metal–phenolic networks

2.1 Chemistry of MPN coordination

MPN coordination represents a foundational and evolving field within chemistry that centers on the interaction and assembly of metal ions with phenolic ligands. The polyphenol structure comprises two or more phenolic hydroxyl units linked by stable carbon–carbon or ester bonds.[22] Based on their chemical architecture, polyphenols can be classified into three primary categories: dihydroxyphenols (such as ellagic acid and quercetin), trihydroxyphenols (such as gallic acid, pyrogallol, and baicalein), and mixed dihydroxyphenol–trihydroxyphenol systems (such as tannic acid and epicatechin gallate). The presence of phenolic hydroxyl groups and aromatic rings enables polyphenols to assemble with various metal ions, molecules, and substrates through both covalent interactions (including Michael addition and Schiff base reactions and coordination interactions) and non-covalent interactions (including hydrogen bonding, π–π stacking, and electrostatic interactions).[31,32]

Phenolic compounds coordinate with metal ions primarily through their hydroxyl (–OH) and carboxyl (–COOH) groups, with catechol and galloyl groups playing significant roles in this coordination. These interactions enable the formation of supramolecular networks that combine the bioactive properties of polyphenols with the specific functionalities of metal ions. Polyphenols are recognized for their ability to coordinate with a wide range of metal ions, such as Cu^{2+}, Fe^{3+}, Zr^{4+}, Ti^{4+}, Zn^{2+}, Fe^{2+}, and Al^{3+}, which plays a crucial role in nature for plant pigmentation and the cycling of cationic nutrients. These complexes exhibit varying stoichiometries (such as mono-, bis-, and tris-complexes), which are influenced by factors including pH, metal ion valence, and the molar ratio of metal ions to phenolic groups.[33] The coordination processes depend not only on the specific polyphenol and metal ion species involved but are also primarily governed by pH conditions.[34,35]

The coordination process is highly sensitive to the pH of the solution. Under alkaline conditions, phenolic hydroxyl groups are easily deprotonated to form phenolate anions. These anions have a high charge density on the oxygen atom, which facilitates strong coordination assembly with metal ions. The coordination state can be adjusted from weak (acidic) to strong (basic). Under alkaline conditions, deprotonation of phenolic hydroxyl groups exposes oxygen centers with high electron density, which facilitates coordination assembly with metal ions.[36] Fig. 2 illustrates the effect of coordination density on coating performance. Low coordination density produces a loosely connected MPN with higher gas and moisture permeability, limited interfacial coordination with the food substrate, and partial microbial surface interaction. In contrast, optimized coordination density results in an interconnected MPN with enhanced coating-substrate coordination, reduced gas and moisture permeability, and restricted microbial contact and activity, supporting improved barrier and preservation functionality.

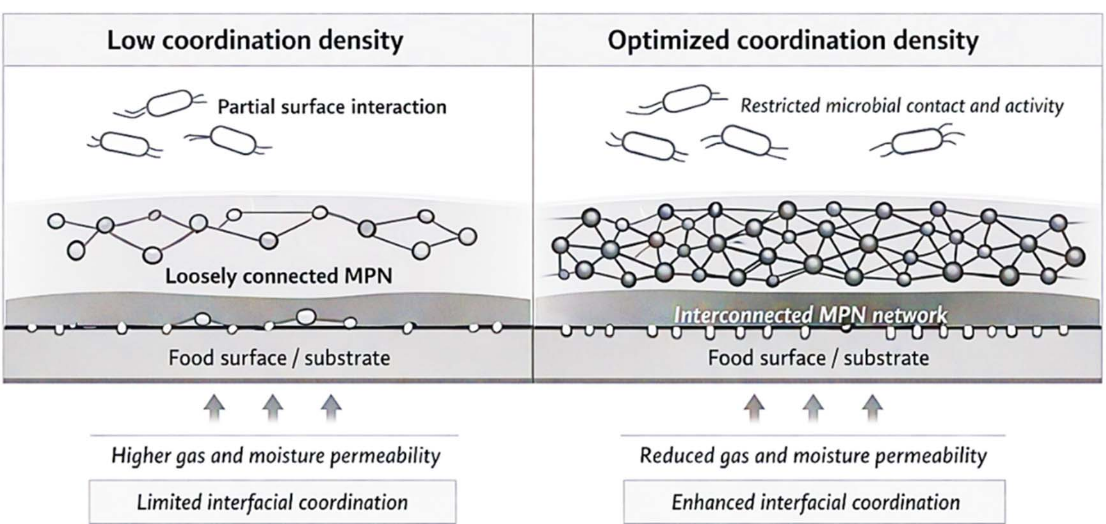

Fig. 2 Structure–function relationship in metal–phenolic network coatings.

2.2 Physicochemical properties relevant to edible coatings

Edible coatings have emerged as a highly effective and safe technology for preserving fresh fruits. They work by limiting gas exchange, which delays the ageing process of fruits during storage.[37] Edible coatings consist of thin material layers applied to food products, usually by dipping or immersion. These coatings function as semi-permeable barriers that shield products from moisture, oxygen, and carbon dioxide. By doing so, they help minimize oxidation processes, slow down respiration rates, and prevent moisture loss, ultimately extending the shelf life of the coated products.[38] Many coatings are enriched with antimicrobial compounds or chitosan, which directly inhibit bacterial and fungal growth by disrupting cell membranes or carrying out other direct antimicrobial actions.[39]

Substrate coating can be achieved through physical, chemical, or biological techniques, all of which are widely employed for developing bioactive interfaces. Physical adsorption represents an approach for creating bioactive interfaces, whereby molecules are deposited onto substrate materials through various non-covalent interactions, including electrostatic forces, hydrogen bonding, hydrophobic effects, van der Waals forces, and others. Despite being economical and simple to implement, physical adsorption has notable limitations, particularly its weak binding strength, which often results in films that are easily removed. Chemical attachment offers an alternative widely used strategy for fabricating bioactive interfaces, in which molecules are covalently bonded to the material surface in either a controlled directional manner or a random non-directional fashion.[40] The integration of metal–phenolic coordination networks into edible coating systems represents a significant advancement, as the strong, multivalent metal–ligand bonds can radically tune the physicochemical properties of the resulting biopolymer matrix such as structural flexibility, pH-responsive behavior, and excellent thermal stability. The MPN edible coating enhanced the mechanical properties by increasing the tensile strength, stiffness and adhesion of the edible film. In a study by Zhang *et al.* (2024),[41] it was reported that the coating film showed significant enhancement after being cross-linked by the MPN *i.e.* the tensile strength increased significantly and the UV light blocking reached up to 99% (1% light transmission) across the 200–400 nm range, while protection of light-sensitive food components achieved up to 78.1% lutein retention following 10 hours of intense light exposure. MPNs inherently possess universal adhesion to virtually any substrate due to the multivalent coordination interactions (metal–ligand, π–π stacking, and H-bonding), which ensures that coating forms a continuous, stable layer on the food surface, preventing peeling or flaking during handling.[19] The coordination of metal ions (such as Fe^{3+} or Al^{3+}) with the polar groups (–OH and –COOH) of the base polymer (like carboxymethyl cellulose) effectively consumes these hydrophilic sites and the coating surface becomes more hydrophobic, indicated by a higher Water Contact Angle (WCA). This is crucial for minimizing moisture loss from the food product.[42] In addition, the MPN used in coating formed a tight cross-linked network that improves the thermal stability of the composite film which is beneficial for food exposed to varied temperatures (Table 1).[43]

3. Functional mechanisms of MPN edible coatings

3.1 Antimicrobial pathways

Coordinated metal ions and phenolic ligands at the food surface interact together to provide the antibacterial efficacy of MPN edible coatings (Table 2). Metal ions cause additional stress by disrupting cellular homeostasis, while phenolic chemicals are known to impair microbial metabolism by membrane instability, protein binding, and enzyme inhibition. These effects are concentrated at the produce interface when integrated into an MPN structure, which eliminates the need for artificial preservatives by generating a hostile milieu for pathogenic microbes and spoiling. Other edible coating systems intended to regulate microbial growth in minimally processed foods have been shown to exhibit similar surface-mediated antimicrobial action.[52,53]

Additionally, MPN coatings function as physical barriers that restrict moisture availability and nutrient transfer at the surface, hence impeding microbial growth. When MPNs are mixed with polysaccharide or protein matrices, this barrier effect intensifies and further limits oxygen transfer and microbial access to the substrate.[54,55] According to recent research, metal–phenolic coordination improves coating adherence and persistence, enabling antibacterial activity to be sustained during storage as opposed to quickly declining after application.[45]

Certain MPN systems show regulated phenolic compound release beyond surface contacts, prolonging antimicrobial activity over time. In line with findings from other natural antimicrobial coating formulations, this prolonged action has been demonstrated to lower overall microbial counts and postpone spoiling across a variety of food systems.[56,57] MPNs can be tailored to various produce types and microbiological problems by adjusting metal type, ligand chemistry, and coating thickness.

3.2 Antioxidant mechanisms

Oxidative degradation is one of the key factors in impairing the post-harvest quality of fresh produce, including the color, texture, nutritional value, and membrane integrity. MPN edible coatings address these changes by compensating for oxidative reactions at the food source rather than from bulk antioxidant additives. MPNs contain phenolic ligands that are capable of decomposing radicals and can neutralize reactive oxygen species before oxidative damage occurs in the tissues. This locally controlled modulation of oxidative stress is particularly relevant in the case of climacteric fruits and high-respiration foods, where reactive oxygen species bind rapidly during storage.[58]

In MPN systems, the coordination of metal ions and phenolic groups stabilizes the antioxidant properties of the coating and thus prevents premature oxidation of phenolic

Table 1 Research evidence of physicochemical properties of MPNs relevant to edible coatings

Phenol	Metal	Food material	Film	Physiochemical properties	References
(−)-Epigallocatechin-3-gallate (EGCG)	Fe^{3+}	Soy protein	Pectin coating	Reduced surface hydrophobicity and improved foaming properties	44
(−)-Epigallocatechin-3-gallate (EGCG)	Fe^{3+}	Strawberries	Spray deposited	It has an effective, scalable, and biocompatible strategy for extending shelf life and reducing postharvest food waste	45
(−)-Epigallocatechin-3-gallate (EGCG)	Zn^{2+}	Strawberries	Spray deposited	The system exhibits considerable promise as an effective, industrially translatable, and physiologically benign platform for ameliorating storage stability and attenuating postharvest waste streams	45
Tannic acid (TA)	Fe^{3+}	Passion fruit	Pectin coating	Significantly reduces the water vapor permeability of the polyethylene (PE) film	46
Tannic acid	Fe^{3+}	Golden passion fruit	Pectin/sodium alginate (PS)	Retarding the ageing process, a reduction in weight loss and a substantial improvement in water retention capacity	47
Tannic acid	Fe^{3+}	Mango fruit	Fish gelatin (FG)-based MPN coatings	The preservation studies revealed that coated samples exhibited markedly reduced weight loss and better retained firmness throughout storage. The treatment effectively slowed the progression of color degradation and limited oxidative stress to cellular membranes, ultimately extending the functional shelf life of the produce	48
Tannic acid	Fe^{3+}	Passion fruit	Sodium alginate (SA) films	The coating significantly reduced weight loss and prevented the shriveling of passion fruit during storage	49
Polyphenol	Titanium (Ti)	Food packaging	Gelatin	It improves film hydrophobicity, as demonstrated by water contact angles between 115.3° and 131.9° and water solubility values ranging from 31.5% to 33.6%	41
Protocatechuic acid (PCA)	Fe^{3+}	Food packaging material	Sodium alginate based films	Food packaging film exhibiting antioxidant, antimicrobial, and hemocompatible properties	43
Procyanidin (PC)	Zn^{2+}	Pork preservation and food packaging	Tilapia gelatin films	The film effectively inhibited bacterial proliferation and reduced the accumulation of total volatile basic nitrogen (TVB-N) and thiobarbituric acid reactive substances (TBARS), thereby extending the refrigerated storage life of pork	50
Ferulic acid	Cu^{2+}	Blueberry and cherry	Carrageenan-based film	The coating proved highly effective for keeping fresh fruit safe from contamination and well preserved throughout the supply chain	51

compounds. This stability allows for sustained antioxidant activity over longer storage periods, as is the case in metal–phenolic coatings of mangoes and other high-moisture fruits.[47] MPN coatings retain the membrane structure and delay softening and browning processes by limiting oxygen diffusion and reducing peroxidation at the tissue interface.

Similar antioxidant effects have been documented in edible coatings made with biopolymers and natural extracts; improvements in chemical and sensory stability were associated with decreases in oxidative indicators.[59,60] By incorporating antioxidant action directly into the coating network instead of depending only on diffusible chemicals, MPNs expand on this idea. According to Huang *et al.* (2025),[61] recent viewpoints emphasize the wider significance of metal–phenolic coordination in agri-food systems, pointing out its capacity to connect molecular antioxidant activity with macroscopic barrier performance. Because of these characteristics, MPN coatings are ideal for produce that needs long-term oxidative protection in a variety of storage environments (Table 3).

Table 2 Functional roles of MPNs in edible coatings and underlying mechanisms

Functional role	Dominant mechanism	Representative metal–phenol pairs	Food-relevant outcome
Antimicrobial activity	Disruption of microbial membranes; controlled metal-ion release; modulation of oxidative stress	Fe^{3+}–tannic acid; Zn^{2+}–catechol	Suppressed microbial proliferation and delayed spoilage
Antioxidant protection	Free-radical scavenging and transition-metal chelation	Fe^{3+}–gallic acid; Cu^{2+}–polyphenols	Reduced lipid oxidation and improved color stability
Barrier enhancement	Network densification and reduction of polymer free volume	Fe^{3+}–EGCG; Al^{3+}–tannins	Lower oxygen and moisture transmission
UV shielding	π–π interactions and metal–ligand charge-transfer absorption	Fe^{3+}–catechol	Protection of light-sensitive pigments and nutrients
Interfacial adhesion	Multidentate coordination and hydrogen-bonding interactions	Fe^{3+}–tannic acid	Improved coating adhesion and stability on produce surfaces

3.3 UV-blocking and barrier properties

UV rays also stimulate oxidative processes, the dehydration of pigments and oxidative degradation in F&V, which results in loss of quality when stored and sold. MPN edible coatings have inherent anti-counter-reactive properties: optically and structurally coordinated phenolic complexes are used as a barrier against these effects. In addition, phenolic ligands emit ultraviolet light at several wavelengths, and metal coordination decreases the attenuation of UV light by stabilizing the conjugated particles that absorb photon energy as heat rather than allowing photochemical reactions.[62,63]

UV protection is associated with good barrier performance in MPN coatings. The dense coordination network that forms at the surface of the produce reduces the permeability of oxygen and moisture and inhibits photo-induced oxidation and loss of water. Among protein- and polysaccharide films with metal–phenolic interactions, gas barrier properties were improved and the coatings are more resistant to light-induced degradation than unmodified biopolymer coatings.[45] This double function is particularly useful in light-sensitive fruits such as berries and grapes, where surface oxidation and pigment instability are rapid.

Recent literature has also shown that some metal oxides can help the spontaneous formation of MPN structures, increasing photoprotective activity and suppressing rogue photoreactivity at the interface.[64] Similar UV-blocking has been observed in food-protected transparent polymer films and serves to emphasize the need for low light attenuation without disturbing sight.[65] MPN edible coatings are a carefully balanced product solution for storage and selling fresh produce exposed to light by combining UV protection with gas and moisture barrier functions.

4. Fabrication and application methods

The formation of MPNs relies on coordination bonds between electron-rich oxygen centers in phenolic compounds and electron-deficient metal ions.[61] Polyphenolic compounds contain multiple hydroxyl groups (–OH) attached to aromatic rings, which can undergo deprotonation under appropriate pH conditions to form phenolate anions. These negatively charged oxygen atoms serve as Lewis bases, donating electron pairs to metal ions (Lewis acids) to form coordinate covalent bonds.[61] The coordination geometry and stoichiometry of metal–phenol complexes depend on several factors, including the oxidation state of the metal ion, the number and spatial arrangement of phenolic hydroxyl groups, and the pH of the assembly medium.[66] Common coordination complexes include mono-complexes (1 : 1 metal-to-ligand ratio), bis-complexes (1 : 2 ratio), and tris-complexes (1 : 3 ratio), with the specific stoichiometry influenced by metal valency and reaction conditions.[66]

The pH of the assembly environment plays a critical role in MPN formation by controlling the deprotonation of phenolic hydroxyl groups and the speciation of metal ions.[61] Under acidic conditions, phenolic groups remain predominantly protonated, limiting their coordination capacity.[66] As pH increases, deprotonation proceeds, enhancing the nucleophilicity of oxygen atoms and promoting coordination to metal centers.[36] For most MPN systems, assembly occurs optimally under neutral to slightly alkaline conditions (pH 7–9), where phenolic groups are sufficiently deprotonated while metal ions remain soluble and available for coordination.[49] However, excessively high pH can lead to metal hydroxide precipitation, competing with MPN formation.[61] The pH-dependent nature of MPN assembly has

Table 3 Influence of metal ion selection on coating performance

Metal ion	Coordination strength	Stability in aqueous media	Functional implications
Fe^{3+}	High	Moderate–high	Strong adhesion and UV blocking
Zn^{2+}	Moderate	High	Antimicrobial and food-safe
Cu^{2+}	High	Moderate	Enhanced antimicrobial action and migration concerns
Al^{3+}	High	High	Dense networks and limited bioactivity

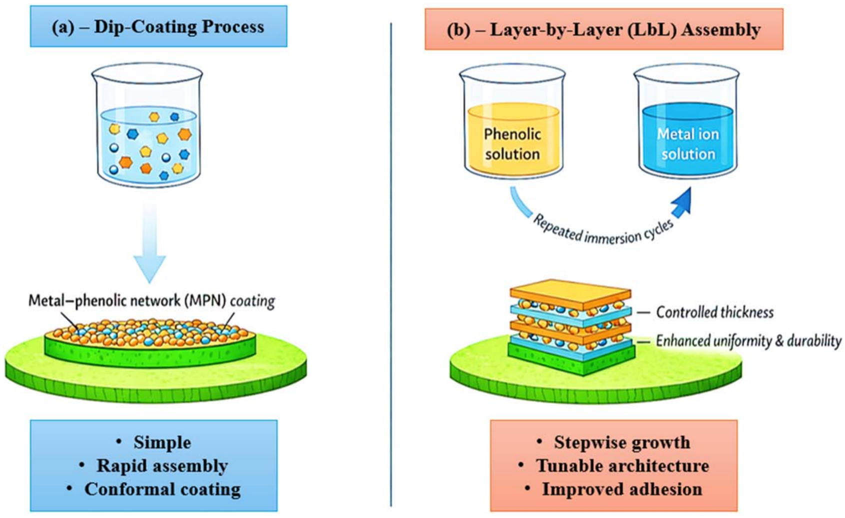

Fig. 3 Schematic illustration of metal–phenolic network (MPN) coating fabrication on food or biopolymer surfaces using (a) dip-coating and (b) layer-by-layer (LbL) assembly.

been exploited for creating pH-responsive materials and controlled release systems.[17]

4.1 Dip-coating and layer-by-layer assembly

Dip-coating (DP) and Layer-by-Layer (LbL) assembly are two of the most commonly employed approaches to make metal–phenolic network edible coatings, wherein they are highly stable and easy to control and can be applied to irregular food surfaces. Dip-coating is done by immersing a material successively or simultaneously in mixtures containing phenolic ligands and metal ions, whereby the product can be coordinated immediately at the surface. This leads to network formation because phenolic groups have a particularly strong affinity for multivalent metal ions and are therefore able to be quickly assembled, without harsh processing conditions[66,67] (Fig. 3).

LbL assembly allows for more control as the steps of phenolic and metal deposition are separated, resulting in more uniform and tunable coating designs. Each immersion cycle generates a separate coating thickness that allows for the control of barrier properties, mechanical stability, and function. This stepwise growth process has been widely applied in multilayers, where the final structure is determined by interfacial interactions as opposed to bulk mixing.[68,69] LbL assembly is especially beneficial for MPN coatings and promotes adhesion and durability during humid storage, where loosely bound coating may otherwise deteriorate.

According to recent research, controlled deposition of ultrathin MPN layers can greatly improve surface functionality without changing food products' sensory qualities.[70] Localized coating production and selective surface modification are made possible by advances in spatiotemporal control of phenolic coordination, allowing for customized application across a variety of produce types.[71] In post-harvest systems, these manufacturing procedures offer a basis for scalable and repeatable MPN coating techniques.

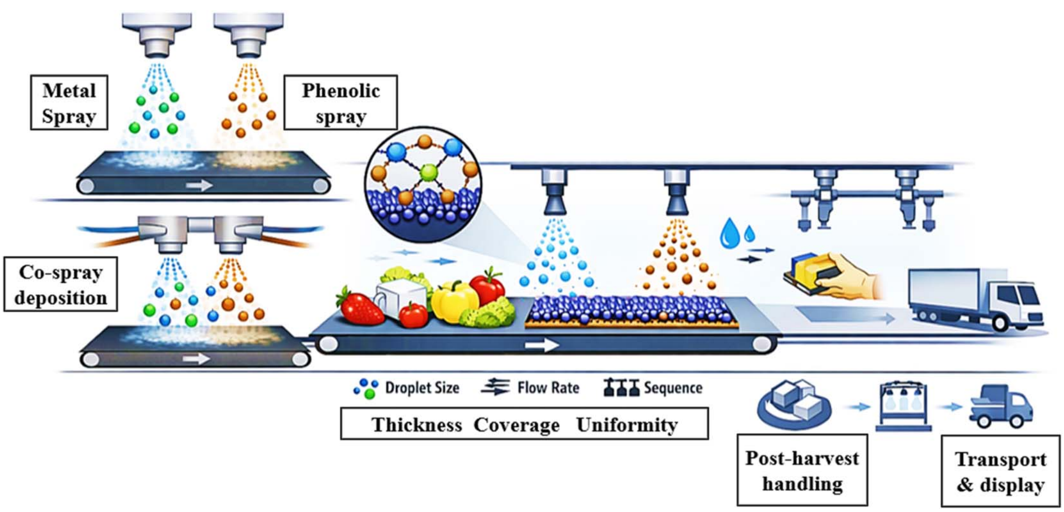

Fig. 4 Schematic illustration of spray-coating-based deposition of metal–phenolic network coatings for industrial scalability.

4.2 Spray-coating for industrial scalability

Spray-coating is an economical method for applying metal–phenolic network coatings on scales relevant to post-harvest handling and industrial processing (Fig. 4). Spray deposition, unlike immersion, allows for coatings to be formed on moving substrates and irregular surfaces with less solution consumption and shorter processing cycles. The formation of MPNs during spraying is mediated by interfacial coordination, and atomized phenolic ligands and metal ions are quickly coupled at contact, resulting in near instantaneous network development.[72]

Control over spray parameters such as droplet size, flow rate and deposition sequence has direct impacts on coating thickness, surface coverage, and uniformity. Specifically, metallic and phenolic solutions are also sequentially sprayed, allowing stepwise network growth, similar to LbL assembly, while co-spraying alone yields faster coverage of thinner coatings. Several spray-assembled MPN systems have been studied for the presence of controlled deposition, in particular for dynamic or high-humidity MPN systems which provide mechanically stable films that are highly adhesion-oriented.[73] These qualities are especially relevant when fresh produce is being handled, transported and displayed.

Scalability-wise, spray-coating fits in nicely with the industrial machinery now in use for post-harvest treatments, waxing, and sanitization. Additionally, phenolic-based surface chemistries show resilience to changes in processing conditions, enabling reliable coating production without strict environmental control.[74] As long as formulation stability and regulatory restrictions are taken care of, MPN spray-coating's potential transfer from lab research to commercial food preservation systems is supported by its ability to be included in continuous processing lines.

4.3 Hybrid MPN–biopolymer composite coatings

Hybrid coatings with metal–phenolic matrices interacting with biopolymer matrices are a useful way to combine interfacial functionality and bulk mechanical stability. Polysaccharides, proteins, and polynucleotides are biopolymers that provide flexibility, film making capability, and affinity to food systems, while MPNs provide surface adhesion, antimicrobial activity, and oxidative resistance. The metal–phenolic interaction in polymeric networks is a dynamic point of cross-linking that provides a stronger, more edible composite structure.[75]

Through coordination-driven reinforcement, the addition of MPNs to biopolymer matrices alters mechanical response, gas permeability, and moisture transport. Reversible metal–ligand bonding, which permits stress dissipation and network reorganization in response to environmental changes, is the source of these effects. Research on a variety of material systems shows that adding MPNs as fillers or interfacial binders improves barrier performance and durability, demonstrating their potential to stabilize coatings during handling.[18,76]

Hybridization also influences functional performance by controlling the mobility and availability of phenolic components. Rather than rapid diffusion or leaching, phenolics remain partially immobilized within the composite matrix, enabling sustained antimicrobial and antioxidant action at the food surface. This behavior aligns with observations from broader studies on antimicrobial MPN systems, where composite architectures extend functional longevity compared with single-component coatings.[18] For edible applications, such hybrid designs allow tuning of coating thickness, flexibility, and sensory impact while retaining surface activity, making MPN–biopolymer composites a versatile platform for fresh produce preservation. Fig. 5 illustrates the conceptual transition of MPN coating processes from laboratory-scale batch operations to industrial-scale continuous application. At the laboratory scale, MPN coatings are prepared *via* batch-wise solution formulation followed by small-volume dip or spray application and ambient or controlled drying. The industrial-scale schematic represents a continuous workflow comprising conveyor-based product feeding, spray-assisted MPN deposition, controlled drying or setting, and post-coating handling and packaging. The schematic in Fig. 5 emphasizes process continuity during scale-up while retaining consistent coating principles, without implying performance enhancement or optimization.

5. Applications for fresh produce preservation

F&V are rich in active compounds and miscellaneous nutrients that play an important role in human health. However, post-

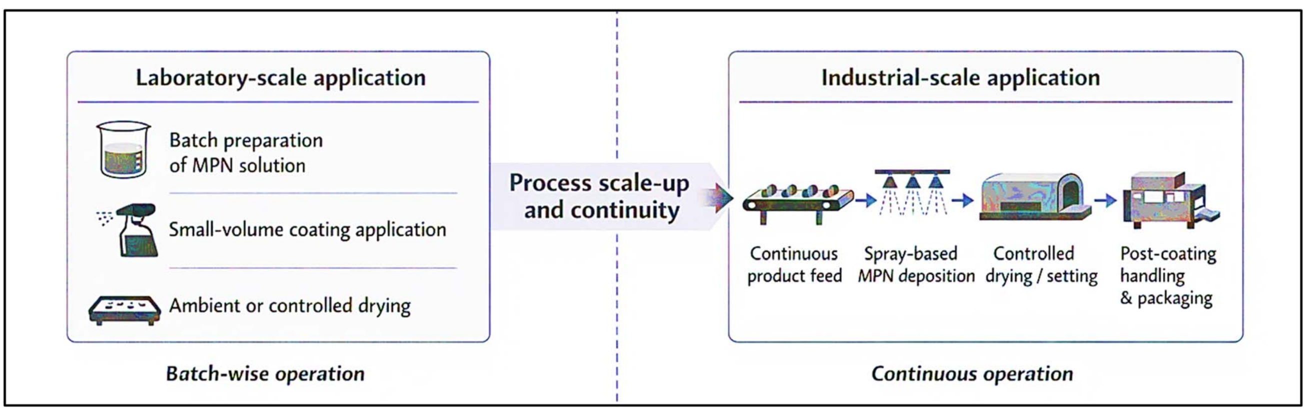

Fig. 5 Transition from laboratory-scale to industrial-scale MPN coating application.

harvest microbial infections not only reduce their economic value but also cause food safety risks to human health. Although traditional chemical preservatives can effectively alleviate these problems, their toxicity may remain on F&V and pose potential risks to consumers' health. Due to the green consumerism trend that limits or ceases the use of suspicious synthetic chemicals, bioactive packaging materials with antibacterial properties have drawn increasing attention. Currently, various endogenous antimicrobials including metal nanoparticles,[77] natural antimicrobials,[78] and organically synthesized antimicrobials[79] have been widely investigated as edible packaging materials. However, the protective functions of these natural biopolymers are still not sufficient due to their moderate antibacterial and antioxidant properties, weak water resistance, and limited mechanical strength.[46,80] Therefore, using MPNs is regarded as a promising strategy to address this problem.[51,61,81,82] For edible packaging applications for F&V, MPNs are typically designed in four types: nanoparticles,[81] hydrogels,[83] nano-capsules,[84] and films (Fig. 6).[49]

5.1 Fruits

Metal–phenolic systems for fruit preservation primarily utilize Fe^{3+} or Zn^{2+} coordinated with polyphenolic compounds such as tannic acid (TA), epigallocatechin gallate (EGCG), or ferulic acid (FA), often integrated into biopolymer matrices including chitosan (CS) or sodium alginate (SA). For apples, MPN films containing Fe^{3+}, fisetin, zein, and nanoparticles (ZnO/TiO_2) have been developed, which decreased the browning index, inhibited weight loss, and suppressed microbial growth.[22] In blueberry preservation, MPN films and hydrogels (*e.g.*, Fe^{3+}–anthocyanin or Zn^{2+}–chlorogenic acid complexes) have been investigated, resulting in increased firmness, inhibited weight loss, and reduced decay rates.[51,83,85–87] Strawberries have been preserved using spray-deposited coatings (Fe^{3+}–TA or Zn^{2+}–EGCG), which provide excellent antibacterial and antioxidant properties, delaying spoilage by up to 1.3-fold and retaining firmness.[45,82]

For mangoes, MPNs have been applied as coatings (Fe^{3+}–TA with fish gelatin) or films, which delayed yellowing, reduced lipid peroxidation damage, and retained essential nutrients.[47,48] MPN films consisting of Zn^{2+} and tea polyphenols applied to bananas resulted in inhibition of enzymatic browning and biofilm formation, effectively extending shelf life.[82] For citrus fruits (oranges and tangerines) and passion fruit, MPN coatings and films enhanced water retention capacity, decreased shrinkage, and retained bioactive qualities including vitamin C and total phenolic content.[43,46,81,88]

5.2 Vegetables

For vegetables, MPN edible packaging studies in the literature are fewer than those on fruits. The present ones mainly focus on retaining structural integrity and preventing microbial contamination, particularly in "fresh-cut" or highly perishable varieties. For preservation of cherry tomatoes, MPN films composed of Cu^{2+}/CGA or Fe^{3+}/TA were integrated with carrageenan or soy protein isolate.[47,51,83,89] Their results included a 3-fold extension of shelf life, stable total soluble solids, better appearance preservation and inhibited weight loss. For fresh-cut lotus root, an MPN film including Fe^{3+}, fisetin, zein, and nano-oxides (ZnO/TiO_2) was studied[22] and a decreased browning index, inhibited microbial growth, and retained hardness of the vegetable were observed. When an MPN film containing ZnONPs and neem essential oil in a chitosan matrix is applied, carrots had inhibited weight loss and a superior antibacterial effect specifically against *E. coli*.[90]

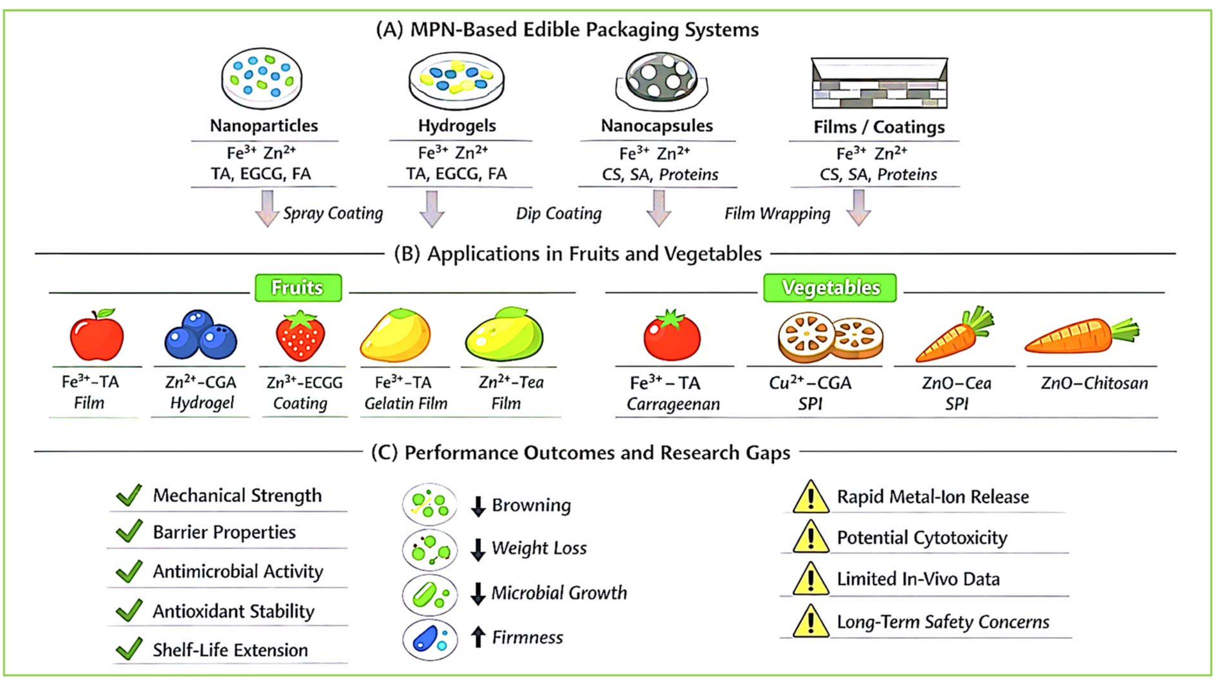

Fig. 6 Applications of MPN based edible packaging for fresh produce preservation.

5.3 Performance evaluation

On inspecting Table 4, it can be concluded that the use and development of MPN systems for F&V edible packaging is a very hot topic due to recent studies on F&V. The number of studies would increase at an escalating rate, with many unexamined types of F&V. In most studies, Fe^{3+}/Zn^{2+} with tannic acid or flavonoids were integrated into polysaccharide/protein films, enhancing mechanical and barrier properties, antimicrobial activity, and oxidative stability, with broad quality and shelf-life improvements. Despite the significant antimicrobial effect of MPNs, they may present several limitations, including the rapid release of metal ions, cytotoxicity, and potential adverse effects on human health.[47] Although some studies presented *in vitro* results about these concerns,[40,78,83,91] most of them were lacking. Therefore, future studies might focus on these aspects by further analyzing with *in vivo* experiments.

5.4 Comparative analysis of MPN-based coatings with conventional edible coatings

Traditional edible coatings have been widely utilized in the food industry for decades, primarily consisting of lipid-based materials (beeswax, carnauba wax, and shellac), polysaccharides (chitosan, starch, alginate, pectin, and cellulose derivatives), proteins (whey protein, casein, gelatin, and soy protein), and composite formulations combining these components.[61,101] Beeswax coatings, one of the most commercially successful edible coatings, have been extensively applied to citrus fruits, apples, and cucumbers to reduce moisture loss and extend shelf life by creating hydrophobic barriers.[102,103] Similarly, chitosan-based coatings have gained prominence due to their inherent antimicrobial properties, biodegradability, and film-forming capacity, making them attractive alternatives to synthetic packaging materials.[104] Polysaccharide-based coatings such as alginate, pectin, and carboxymethyl cellulose have been utilized for their excellent barrier properties against oxygen and carbon dioxide, while protein-based coatings offer good mechanical strength and flexibility.[105]

Comparing barrier properties, conventional edible coatings and MPN-based systems exhibit distinct performance characteristics. Lipid-based coatings such as beeswax provide excellent moisture barriers due to their hydrophobic nature, effectively reducing water vapor transmission rates and preventing weight loss in fresh produce.[103] However, these coatings offer limited protection against oxygen and microbial penetration, restricting their effectiveness in preventing oxidative deterioration and pathogen contamination.[102] In contrast, MPN-based coatings demonstrate multifunctional barrier properties, simultaneously providing moisture resistance, oxygen barriers, and UV light blocking capabilities.[49] The UV light shielding capacity of MPNs can reach up to 99% light transmission blocking across the 200–400 nm range, offering superior protection for light-sensitive bioactive compounds compared to conventional wax or polysaccharide coatings.[106,107]

Polysaccharide-based coatings such as chitosan and alginate provide moderate moisture barriers but excel in gas permeability control, making them suitable for regulating respiration in fresh produce.[108] However, their hydrophilic nature limits their moisture resistance, often necessitating combination with lipid components to achieve adequate water vapor barriers. MPN-based coatings address this limitation through coordination-driven cross-linking, which enhances network density and reduces permeability without requiring lipid incorporation.[107] Studies have demonstrated that MPN-chitosan composite films exhibit water contact angles ranging from 115.3° to 131.9°, indicating substantially improved hydrophobicity compared to unmodified chitosan films.[109]

Antimicrobial activity represents a critical differentiating factor between conventional coatings and MPN-based systems. Beeswax and other lipid-based coatings possess negligible inherent antimicrobial properties and rely solely on physical barrier effects to reduce microbial contamination.[110] Chitosan-based coatings demonstrate moderate antimicrobial activity attributed to electrostatic interactions between positively charged amino groups and negatively charged microbial cell membranes, with effectiveness varying based on molecular weight, degree of deacetylation, and pH conditions.[111] However, chitosan's antimicrobial efficacy diminishes significantly at neutral or alkaline pH, limiting its application range.

MPN-based coatings offer superior and broader-spectrum antimicrobial activity through synergistic mechanisms combining metal ion cytotoxicity, polyphenol-mediated membrane disruption, and reactive oxygen species generation.[50,100] Fe^{3+}-based MPNs demonstrate bacterial inhibition rates exceeding 90% against common foodborne pathogens including *Escherichia coli*, *Staphylococcus aureus*, and *Listeria monocytogenes*, substantially outperforming chitosan or beeswax coatings.[112] Zn^{2+} and Cu^{2+}-based MPNs exhibit even higher antimicrobial potency, with minimum inhibitory concentrations significantly lower than those of conventional preservatives, while retaining pH-independent activity across a wide range of food matrices.[113] Furthermore, MPN-based systems demonstrate antifungal efficacy against spoilage fungi such as *Botrytis cinerea*, *Penicillium* species, and *Aspergillus* species, effectively reducing decay rates in F&V by 40–60% compared to conventional coatings.[114,115]

Antioxidant functionality represents another area where MPN-based coatings demonstrate clear advantages over conventional systems. Lipid-based coatings such as beeswax and carnauba wax possess no antioxidant activity and may actually accelerate lipid oxidation under certain conditions due to trace pro-oxidant metal contaminants.[116] Polysaccharide- and protein-based coatings similarly lack inherent antioxidant properties, though they can be fortified with external antioxidant additives such as ascorbic acid, tocopherols, or plant extracts.[117] However, these incorporated antioxidants may leach or degrade during storage, diminishing long-term protection. In contrast, MPN-based coatings possess intrinsic and stable antioxidant activity derived from polyphenolic components, which are structurally integrated into the coordination network.[50,100] The metal–phenol coordination not only stabilizes polyphenols against degradation but also can enhance their radical scavenging capacity through electronic effects.[118] MPN coatings containing tannic acid, EGCG, or chlorogenic acid

Table 4 The applications of MPNs for fresh produce preservation[a]

	MPN coating composition	Application form	Effects on food products	References
Fruits				
Apple	Fe^{3+}, fisetin, zein, citral, CS, ZnONPs, TiO_2NPs, and SA	Film	Decreased browning index, inhibited weight loss, suppressed microbial growth, retained hardness, and inhibited total phenolic content decrease	22
Banana	Zn^{2+} and tea polyphenols	Film	Inhibited enzymatic browning and spoiling and biofilm formation, retained freshness, reduced weight loss, and extended shelf-life	92
Blueberry	Fe^{3+}, anthocyanin, cellulose nanofiber (CNF), and SA	Film	Inhibited weight loss, increased firmness index and total soluble solids reduced total phenolic content decrease, retained total monomeric anthocyanin, and reduced percent polymeric color leaching	85
Blueberry	Cu^{2+}, FA, and carrageenan	Film	Better appearance preservation, inhibited weight loss, and retained hardness, pH, and total soluble solid content	51
Blueberry	Fe^{3+}, TA, CMC, SPI, and Eos	Film	Better appearance preservation, inhibited weight loss, and retained hardness and total phenolic content	51
Blueberry	Zn^{2+}, CGA, quaternary ammonium insect CS, and oxidized pullulan	Hydrogel	Retained good appearance, inhibited weight loss, decreased decay and respiration rates, delayed pH increase, delayed firmness decrease, and inhibited bacterial growth	82
Blueberry	Fe^{3+}, konjac glucomannan, xanthan gum, SPI and TA	Film	Better appearance preservation, inhibited weight loss, retained total soluble solid content and stable pH, and reduced total viable count	87
Cherry	Cu^{2+}, FA, and carrageenan	Film	Better appearance preservation, inhibited weight loss, delayed hardness, and retained pH and total soluble solids	93
Cherry	Zn^{2+}, CGA, quaternary ammonium insect CS, and oxidized pullulan	Hydrogel	Retained good appearance, inhibited weight loss, decreased decay and respiration rates, delayed firmness decrease, and inhibited bacterial growth	49
Cherry	Cu^{2+}, FA, and carrageenan	Film	Better appearance preservation, inhibited weight loss, delayed hardness, and retained pH and total soluble solids	51
Fresh-cut apple	Fe^{3+}, fisetin, zein, citral, CS, ZnONPs, TiO_2NPs, and SA	Film	Decreased browning index, inhibited weight loss, increased hardness, and reduced total plate count	22
Fresh-cut apple	Fe^{3+}, TA, CMC, SPI, and Eos	Film	Better appearance preservation, inhibited weight loss, and retained hardness and total phenolic content	94
Fresh-cut pear	Fe^{3+}, TA, SPI, and CMC	Film	Better appearance preservation, inhibited weight loss, and retained hardness and total phenolic content	80
Golden passion fruit	Fe^{3+}, TA, PE, and SA	Coating	Inhibited weight loss, decreased shrinkage index, and enhanced water retention capacity	17
Kiwi	Fe added CNF, curcumin, and CS	Coating	Better appearance preservation, inhibited weight loss and respiration rate, retained firmness and physicochemical properties (pH and TA), and reduced mesophilic bacteria proliferation	95
Mango	Fe^{3+}, TA, and fish gelatin (FG)	Coating	Inhibited weight loss, retained firmness, delayed yellowing, reduced lipid peroxidation damage and extended shelf life	40
Mango	Fe^{3+}, TA, EOs, microcrystalline cellulose, and CS	Film	Inhibited weight loss, increased soluble solids, and nutrient retention	48
Orange	Fe^{3+}, TA, PVA, quaternary ammonium salt (QAS), and CNF	Film	Retained good appearance, inhibited weight loss, and delayed pH increase	88
Orange	Fe^{3+} and TA	Coating	Better appearance preservation	47
Strawberry	Fe^{3+} and TA	Spray coating	Excellent antibacterial and antioxidant properties, effectively retaining the freshness and extending the shelf life	96
Passion fruit	Fe^{3+}, TA, and PE	Coating	Inhibited weight loss and shrinkage index and enhanced freshnesspreservation	46

Table 4 (*Contd.*)

	MPN coating composition	Application form	Effects on food products	References
Strawberry	Fe^{3+}–EGCG and Zn^{2+}–EGCG	Spray coating	Fe^{3+}–EGCG and Zn^{2+}–EGCG coatings delayed spoilage (1.3-fold). Zn–EGCG: reduced weight loss and retained firmness. Zn–EGCG: better oxidative stability and moisture barrier properties. Fe–EGCG: reduced performance over time	45
Strawberry	Zn^{2+} and tea polyphenols	Film	Inhibited enzymatic browning and spoiling and biofilm formation, retained freshness, reduced weight loss, and extended shelf-life	92
Tangerine	Fe^{3+}, Mo^{6+}, TA, and CS	Film	Inhibited weight loss, delayed hardness, decreased total soluble solids, and retained vitamin C and total phenolic content	97
Vegetables				
Carrot	ZnONPs, neem essential oil, and CS	Film	Inhibited weight loss and enhanced antibacterial effect on *E.coli*	98
Cherry tomato	Cu^{2+}, CGA, gelatin, and carrageenan	Film	Enhanced appearance preservation, less weight loss, retained firmness, stable total soluble solids, and 3-fold extension of shelf life	83
Cherry tomato	Cinnamaldehyde, Fe^{3+}, TA^{+}, and κ-carrageenan (KC)	Film	Better appearance preservation, inhibited weight loss, delayed pH increase, and retained hardness	99
Cherry tomato	CMC, SPI, EOs, Fe^{3+} and TA	Film	Better appearance preservation, inhibited weight loss, and retained hardness and total phenolic content	100
Fresh cut lotus root	Fe^{3+}, fisetin, zein, citral, CS, ZnONPs, TiO_2NPs, and SA	Film	Decreased browning index, inhibited weight loss, suppressed microbial growth, retained hardness, and inhibited the total phenolic content decrease	47

[a] Abbreviations: BPQDs, black phosphorus quantum dots; CS, chitosan; CGA, chlorogenic acid; CNF, cellulose nanofiber; CMC, carboxymethylcellulose; CMCS, carboxymethyl chitosan; EGCG, epigallocatechin gallate; EOs, essential oils; FA, ferulic acid; PE: pectin; TA, tannic acid; SA, sodium alginate; SPI, soy protein isolate.

demonstrate DPPH radical scavenging rates of 80–95%, significantly higher than those of fortified conventional coatings.[43,119] This superior antioxidant capacity translates to improved retention of bioactive compounds in coated produce, with studies reporting up to 78.1% lutein retention after 10 hours of intense light exposure and 60–80% vitamin C preservation during extended storage, substantially outperforming beeswax or chitosan coatings.[93,120]

Mechanical properties significantly influence the practical applicability and consumer acceptance of edible coatings. Beeswax coatings exhibit good flexibility and adhesion but suffer from brittleness at low temperatures and melting at elevated temperatures, limiting their application range.[121] Polysaccharide-based coatings generally demonstrate moderate tensile strength (5–50 MPa) but poor elongation at break (<10%), resulting in brittle films prone to cracking during handling and storage.[76] Protein-based coatings offer better flexibility but exhibit moisture sensitivity, with mechanical properties deteriorating significantly under high humidity conditions.[122] MPN-based coatings achieve enhanced mechanical properties through metal–phenol coordination cross-linking, which creates three-dimensional network structures with improved cohesion and structural integrity.[17] Studies report that MPN-reinforced biopolymer films exhibit tensile strengths of 40–80 MPa and elongation at break values of 15–40%, representing 2–3 fold improvements over unmodified polysaccharide films.[123] The coordination cross-links also reduce moisture sensitivity, retaining mechanical stability across relative humidity ranges of 33–84%, compared to conventional protein or polysaccharide films which show 50–70% strength reduction at high humidity.[101] Furthermore, MPN coatings demonstrate excellent adhesion to diverse produce surfaces due to polyphenol-mediated surface interactions, reducing coating detachment during washing or handling compared to wax-based alternatives.[50]

5.5 Metal migration, regulatory considerations, and strategies to minimize exposure

Metal migration from food contact materials represents a critical safety consideration that must be thoroughly addressed before widespread commercial adoption of MPN-based coatings. The potential release of metal ions from coordination networks into food products raises toxicological concerns, particularly regarding cumulative dietary exposure and potential adverse health effects from chronic consumption.[124,125] Unlike conventional edible coatings composed solely of organic polymers, MPN systems inherently contain metal ions as structural components, necessitating rigorous assessment of migration behavior under realistic food storage and handling conditions.[124,125] The coordination bonds between metal ions and polyphenolic ligands, while generally stable, may undergo partial dissociation in response to pH changes, chelating agents, or competing ligands present in food matrices, potentially leading to metal release.[17]

The extent and rate of metal migration depend on multiple factors including the identity and oxidation state of the metal ion, the coordination geometry and stoichiometry of the metal–phenol complex, the cross-linking density of the MPN, and the characteristics of the food product including pH, ionic strength, fat content, and the presence of complexing agents such as organic acids, phosphates, or proteins.[61,100] Acidic foods (pH < 4.5) pose particular challenges, as protonation of phenolic ligands at low pH can destabilize coordination bonds and promote metal release.[124,125] Similarly, foods containing high concentrations of chelating agents such as citric acid, EDTA, or polyphosphates may sequester metal ions from MPNs through competitive coordination, accelerating migration.[124,125]

5.5.1 Health risks associated with metal migration. The toxicological implications of metal migration from MPN coatings vary substantially depending on the specific metal ion employed and the extent of release. Essential trace elements such as Fe^{3+}, Zn^{2+}, and Ca^{2+}, which are commonly utilized in MPN formulations, generally pose lower toxicity risks compared to heavy metals, as these elements are nutritionally required and subject to homeostatic regulation in the human body.[126] However, excessive intake even of essential metals can lead to adverse effects. Iron overload from chronic excessive consumption can cause oxidative stress, liver damage, and increased risk of cardiovascular disease and certain cancers, particularly in individuals with genetic predispositions such as hemochromatosis.[127] The use of transition metals with known toxicity concerns, such as copper and cadmium, in MPN systems requires particularly stringent control of migration. While copper is an essential micronutrient, chronic excessive intake (>10 mg per day) can lead to liver toxicity, particularly in susceptible individuals with Wilson's disease or other disorders of copper metabolism.[128] Cadmium, even at trace levels, poses serious health risks including kidney damage, bone demineralization, and carcinogenicity, with the European Food Safety Authority establishing a tolerable weekly intake of only 2.5 μg per kg body weight.[126,129] Consequently, the use of cadmium in food contact applications is heavily restricted or prohibited in most jurisdictions, making it unsuitable for MPN-based edible coatings despite its favorable coordination chemistry.[100]

Recent risk assessments have evaluated potential dietary exposure from MPN-coated produce in worst-case consumption scenarios. Studies by Chiu *et al.* (2025)[45] measured iron migration from Fe^{3+}–EGCG MPN coatings on strawberries, reporting a maximum release of 2.3 mg Fe per 100 g fruit after 14 days of storage at 4 °C. Assuming daily consumption of 200 g of coated strawberries, this would contribute approximately 4.6 mg iron to daily dietary intake, representing 25–50% of the recommended dietary allowance (8–18 mg per day for adults) but remaining well below the upper tolerable intake level of 45 mg per day.[45] Similarly, Zeng *et al.* (2019)[92] assessed zinc migration from Zn^{2+}–tea polyphenol MPN coatings on bananas, finding a maximum release of 1.8 mg Zn per 100 g fruit, which would contribute 15–20% of the recommended dietary allowance but less than 10% of the upper intake level even with high consumption rates. These assessments suggest that MPNs formulated with essential trace elements at appropriate concentrations pose minimal acute toxicity risks under normal consumption patterns.[124,125]

However, cumulative exposure considerations require careful attention, particularly for populations with high produce consumption or those exposed to metals from multiple dietary and environmental sources.[17] Vulnerable populations including pregnant women, young children, individuals with genetic disorders affecting metal metabolism, and those with compromised kidney or liver function may require additional protection measures.[101,122] Life-cycle exposure assessments incorporating metal intake from MPN-coated foods alongside other dietary sources, drinking water, and environmental exposure are essential for comprehensive risk characterization.[76]

5.5.2 Regulatory framework for metal migration. Food contact materials are subject to stringent regulatory oversight in major jurisdictions including the European Union, the United States, China, and other countries, with specific migration limits established for various metals to ensure consumer safety.[130] In the European Union, Regulation (EC) No 1935/2004 establishes a general framework for food contact materials, requiring that materials do not transfer constituents to food in quantities that could endanger human health or cause unacceptable changes in food composition or organoleptic properties. Specific migration limits (SMLs) for metals in food contact materials are established in Commission Regulation (EU) No 10/2011 and subsequent amendments, with limits varying based on toxicological assessment of each element.[131]

For commonly used MPN metals, EU specific migration limits include aluminum (1.0 mg per kg food), iron (48 mg per kg food), zinc (25 mg per kg food), and copper (5.0 mg per kg food).[131] The United States FDA regulates food contact substances under the Federal Food, Drug, and Cosmetic Act, with migration limits established through food contact notifications (FCNs) or food additive petitions based on safety assessments.[132] The FDA has established action levels and tolerances for various metals in food, including lead (0.1 mg kg^{-1} in fruit juice), cadmium (varies by food type), and arsenic (0.1 mg kg^{-1} in apple juice), though specific migration limits for food contact materials differ from total allowable levels in food.[133]

China's regulatory framework for food contact materials, governed by GB 4806 series standards, establishes specific migration limits for metals including iron (≤50 mg kg^{-1}), zinc (≤25 mg kg^{-1}), copper (≤15 mg kg^{-1}), and chromium (≤0.01 mg kg^{-1} for hexavalent chromium) (NHFPC, 2016; He *et al.*, 2025).[100,134] Testing protocols typically involve migration studies using food simulants representing different food categories (aqueous, acidic, alcoholic, and fatty foods) under defined time–temperature conditions designed to simulate worst-case exposure scenarios.[135]

For MPN-based edible coatings to achieve regulatory approval, comprehensive migration studies must demonstrate compliance with applicable limits across relevant food simulants and actual food products.[88,90] The edible nature of MPN coatings adds regulatory complexity, as the coating is intentionally consumed rather than merely coming into contact with food, potentially requiring assessment under food additive regulations rather than solely as food contact materials.[22] This distinction may necessitate more stringent safety documentation including toxicological studies, metabolic fate assessments, and establishment of acceptable daily intake levels for the complete MPN formulation.[17]

5.5.2.1 Measured migration rates from MPN systems. Recent experimental studies have quantified metal migration from various MPN-based coating systems, providing empirical data to support risk assessment and regulatory evaluation. Chiu *et al.* (2025) conducted comprehensive migration studies on spray-deposited EGCG–Fe^{3+} MPN coatings applied to strawberries, tomatoes, and bell peppers. Using atomic absorption spectroscopy, they measured iron release into food simulants (3% acetic acid for acidic foods and 10% ethanol for aqueous foods) over 10 days at 4 °C and 20 °C. Maximum iron migration was observed in the acidic simulant at 20 °C, reaching 3.2 mg kg^{-1} after 10 days, well below the EU specific migration limit of 48 mg kg^{-1}.[45] Importantly, migration rates in actual strawberry tissue were significantly lower (1.8 mg kg^{-1}) than those in the acidic simulant, suggesting that food matrix effects may reduce metal release compared to worst-case simulant conditions.

Zeng *et al.* (2019) evaluated zinc migration from Zn^{2+}–tea polyphenol MPN films applied to banana peels, measuring Zn^{2+} concentrations in banana pulp using inductively coupled plasma mass spectrometry (ICP-MS) over 14 days of storage at 15 °C and 25 °C. Zinc migration into pulp reached maximum levels of 2.1 mg kg^{-1} at 25 °C, representing less than 10% of the EU migration limit of 25 mg kg^{-1}.[92] Kinetic analysis revealed that migration followed a Fickian diffusion model with apparent diffusion coefficients of 1.2×10^{-12} cm^2 s^{-1} at 15 °C and 3.8×10^{-12} cm^2 s^{-1} at 25 °C, indicating relatively slow metal release kinetics.[92]

Li *et al.* (2025) investigated copper migration from Cu^{2+}–tannic acid MPN nanoparticles incorporated into carboxymethyl cellulose/polyvinyl alcohol composite films. Migration testing using 3% acetic acid and 50% ethanol simulants at 40 °C for 10 days showed a copper release of 0.82 mg kg^{-1} and 0.34 mg kg^{-1} respectively, significantly below the 5 mg per kg EU limit.[88] The substantially lower migration in ethanol compared to acetic acid highlights the pH-dependence of MPN stability, with acidic conditions promoting greater metal release.[88]

Chen and Tang (2024) examined metal migration from chitin nanocrystal films modified with Fe^{3+}–gallic acid MPNs, testing migration into various food simulants including water, 3% acetic acid, 10% ethanol, and olive oil (representing fatty foods) at 40 °C for 10 days. Iron migration was the highest in acetic acid (4.8 mg kg^{-1}), moderate in ethanol (1.2 mg kg^{-1}) and water (0.8 mg kg^{-1}), and negligible in olive oil (<0.1 mg kg^{-1}), confirming that acidic foods represent the worst-case scenario for metal release while fatty foods show minimal migration.[136] All measured values remained well below regulatory limits, supporting the safety profile of MPN-modified films.

Long-term migration studies by Wei *et al.* (2025) tracked iron release from Fe^{3+}–fisetin MPN-coated zein nanoparticles in polysaccharide bilayer films over 60 days at refrigeration (4 °C) and ambient (25 °C) temperatures. Cumulative iron migration plateaued after approximately 30 days, reaching steady-state levels of 3.5 mg kg^{-1} at 4 °C and 6.2 mg kg^{-1} at 25 °C, suggesting that migration is self-limiting rather than continuing indefinitely.[22] This plateau behavior likely reflects establishment of thermodynamic equilibrium between coordinated and free metal ions, reducing ongoing release after initial migration.

Comparative studies by Li *et al.* (2025) evaluated migration from MPN systems utilizing different metal–phenol combinations, including Fe^{3+}–tannic acid, Zn^{2+}–EGCG, Cu^{2+}–quercetin, and Al^{3+}–chlorogenic acid. Migration testing in 3% acetic acid revealed substantial differences among systems: Fe^{3+}–TA (4.1 mg kg^{-1}) < Al^{3+}–CGA (4.8 mg kg^{-1}) < Zn^{2+}–EGCG (8.3 mg kg^{-1}) < Cu^{2+}–quercetin (12.7 mg kg^{-1}), indicating that coordination complex stability varies significantly with metal–ligand pairing.[137] These findings emphasize the importance of selecting metal–phenol combinations with high coordination stability to minimize migration, particularly for acidic food applications.

6. Safety and regulatory considerations

MPN-based packaging offers excellent barrier properties against light, gas, and moisture, is recyclable, allows for easy fabrication into various shapes, withstands high processing temperatures, possesses a rigid structure, enables long-distance transportation, and provides distinctive decorative possibilities.[130,131] However, these advantages come at a considerable cost. The drawbacks include contributions to global warming through carbon dioxide emissions from metal production facilities. Additional safety concerns involve the migration of harmful toxic substances from containers into food products and the depletion of natural resources. Regulatory bodies, such as the European Directorate for the Quality of Medicines and HealthCare (EDQM) and the FDA, set specific release limits (SRLs) for various metals to minimize health risks.[100,130,131,135] Migration assessments are mandatory to ensure that these levels remain within safe thresholds. A balance between both aspects of metal food packaging must be maintained through improved research and policy development. Metal phenolic networks are often designed to be pH-responsive, meaning that they may disassemble more rapidly under acidic conditions (common in many foods such as juices and fruits).[45,130,133,134] While this can enable targeted release of encapsulated beneficial agents, it also means that the release rate of metal components needs careful study and control for different food types.

7. Challenges and future opportunities

MPN edible coatings represent a promising yet still emerging strategy for extending the shelf life and quality of fresh F&V.[45] They are appealing substitutes for traditional postharvest treatments due to their multipurpose qualities, which include antibacterial activity, antioxidant protection, and barrier enhancement.[137] A number of interconnected scientific, technological, legal, and practical obstacles prevent MPN coatings from moving from laboratory study to commercial application. However, developments in food technology and materials science present obvious chances to overcome these constraints and direct further advancements.

The most important factor for MPN-based edible coatings is still safety. Although many of the phenolic ligands employed in MPNs are found naturally in food and are linked to health benefits,[61] their coordination with metal ions can change biological interactions, chemical behaviour, and bioavailability. The possible migration and release of metal ions from the coating into the food during storage and consumption is a major concern.[81] Consuming coated products regularly may result in metal exposure that is beyond legal limits, especially when transition metals are present. Therefore, thorough migration studies under practical handling and storage situations are crucial. Because coordination can affect absorption, metabolism, and excretion pathways, safety assessment must therefore go beyond evaluating individual components to consider coordinated metal–phenolic complexes as functional entities. Given the variety of consumer demographics and the possible interaction of MPNs with gastrointestinal tissues and microbiota, long-term exposure studies including *in vitro* digestion models and *in vivo* investigations are particularly crucial.[79,83,84]

The problem of sensory acceptance, which has a significant impact on consumer adoption, is closely related to safety.[71] Small modifications to flavour, scent, texture, or appearance can lower market acceptance even in cases when coatings are safe and effective. While metal ions can alter surface colour or gloss, some phenolic chemicals can add astringency or bitterness.[74,75] To reduce noticeable alterations, future studies should focus on carefully choosing phenolic ligands and metal ions and precisely controlling coating thickness and homogeneity. Crucially, rather than being viewed as a last validation stage, sensory evaluation ought to be incorporated early into the formation process.

The practical application of MPN edible coatings is mostly dependent on scalability and manufacturing practicality. Although MPN assembly is simple in the lab, strict control over processing factors, including pH, ionic strength, and metal-to-ligand ratios, is necessary for industrial-scale deployment.[45,100,133] Reproducibility in high-throughput settings can be hampered by slight variations in these variables, which can result in uneven coating thickness, uneven surface coverage, and inconsistency in functional performance. Economic considerations can affect viability because it can be expensive to purify and provide phenolic chemicals on a large scale, and using specific metal salts may boost manufacturing costs or sustainability issues.[37–39] Therefore, in order to improve both economic and environmental sustainability, future development should give priority to inexpensive, food-grade phenolics made from agricultural byproducts and environmentally safe metals.

Another crucial prerequisite for commercialisation is compatibility with current postharvest infrastructure. Without significantly increasing processing time, energy consumption, or system complexity, MPN coating procedures must blend in seamlessly with current washing, sorting, and packaging activities. While dip-coating and spray-coating methods are promising, more refinement is needed to handle a variety of product geometries, surface properties, and throughput requirements. Validating scalability and converting laboratory results into commercially applicable techniques requires pilot-scale studies and process modelling.[45,92,130,133]

The design of MPN coatings is made more difficult by the variety of fresh fruits. The respiration rate, surface shape, cuticle composition, and susceptibility to external coatings of F&V are significantly different.[137] As a result, it is doubtful that a single MPN formulation will work everywhere. Produce that is prone to microbial deterioration might benefit from higher antibacterial activity, whereas high-respiration goods might need coatings with increased gas permeability.[54] A thorough grasp of how coordination chemistry controls barrier characteristics, mechanical behaviour, and bioactivity is necessary to tailor MPN composition to particular commodities. Using data-driven design tools and computer modelling to establish strong structure–function links could speed up formulation optimisation and lessen the need for empirical methods.

Insufficient research has been done on long-term stability and performance in practical storage and distribution situations. Coating integrity and functioning can be jeopardised by changes in temperature, humidity, mechanical wear, and light exposure. Thus, extensive research that mimics commercial storage, transportation, and retail settings is required. Furthermore, it is important to carefully assess how MPN coatings interact with local microbial communities. Although antimicrobial actions are desirable, severe disturbance of neutral or helpful microorganisms may change the ecological balance or spoil the dynamics.[36,43,50,52,53,137]

In the future, functionalised and intelligent MPN coatings offer a significant possibility. Adaptive preservation techniques and real-time freshness monitoring may be made possible by stimuli-responsive behaviour, sensor capabilities, and hybrid composite architectures. MPN coatings have a great chance of developing into useful instruments for sustainable fresh food preservation with concerted advancements in materials design, processing, and interdisciplinary cooperation.[94,96,138–140]

8. Conclusion

MPN based edible coatings represent a practical and scientifically grounded approach to improving the post-harvest stability of fresh F&V. By relying on coordination between naturally derived phenolic compounds and food-grade metal ions, these coatings provide combined antimicrobial, antioxidant, and barrier functions within a single, thin layer applied directly to produce surfaces. Reported studies consistently show delayed microbial growth, reduced oxidative damage, and improved retention of visual and textural quality across a wide range of F&V. The performance of MPN coatings is closely linked to their composition, metal–ligand ratio, and application method, highlighting the importance of formulation control for different types of produce. At the same time, issues such as sensory impact, regulatory compliance, and long-term safety require careful consideration before large-scale adoption. Current evidence suggests that appropriate selection of phenolic sources and metal ions can minimize these concerns while maintaining functional effectiveness. Further development of MPN edible coatings will benefit from systematic studies addressing scalability, storage behavior under real supply-chain conditions, and interactions with natural produce microflora. With continued refinement, MPN-based coatings have the potential to support cleaner labeling, reduced post-harvest losses, and more sustainable strategies for fresh produce preservation.

Conflicts of interest

There are no conflicts to declare.

Data availability

Data sharing is not applicable to this article as no new data were created or analyzed in this study. All data discussed in this review are derived from previously published literature, which has been appropriately cited throughout the manuscript.

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