Metal–organic frameworks for active food packaging. A review

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Abstract
Food wastage is a major concern for sustainable health and agriculture. To reduce food waste, classical preservation techniques such as drying, pasteurization, freeze-drying, fermentation, and microwave are available. Nonetheless, these techniques display shortcomings such as alteration of food and taste. Such shortcomings may be solved by active food packaging, which involves the incorporation of active agents into the packaging material. Recently, metal–organic frameworks, a class of porous hybrid supramolecular materials, have been developed as an active agent to extend food shelf life and maintain safety. Here, we review metal–organic frameworks in active packaging as oxygen scavengers, antimicrobials, moisture absorbers, and ethylene scavengers. We present methods of incorporation of metal–organic frameworks into packaging materials and their applications.

Keywords Metal–organic frameworks · Food packaging · Food safety · Scavenger · Absorber · Antimicrobial

Introduction

Around one-third of the food produced for human consumption is lost or wasted, and it has been reported that 59–65% of the food waste can be avoided (Gupta et al. 2021a; Kumar et al. 2021c; Blanke, 2014). Broadly, food can be categorized into plant-based food such as fruits and vegetables, cereal-based products, and animal-based food such as meat-based products. Food undergoes spoilage due to microbial contamination, enzymatic degradation, oxidation, excess of ethylene, uncontrolled temperature, undesirable moisture, and inadequate pH. Several techniques are implemented to avoid food spoilage, maintain quality and prevent wastage throughout the supply chain (Kumar et al. 2021a; de Souza et al. 2018; Gupta et al. 2021b). But currently used techniques are not effective enough and have an adverse effect on the environment (Gupta et al. 2021b; Pandiselvam et al. 2019). One of the potential ways is improving the packaging attributes to reduce the undesirable changes in the food (Singh et al. 2021b; Kumar et al. 2021a). Food packaging plays a critical role in food supply chain and preserving the quality of food (Kumar et al. 2021b). Evolution in food packaging research has led to the exploration of innovative active packaging developed by incorporation of bioactive components, antimicrobial peptides, metal–organic frameworks (MOFs), and many more to achieve desired active packaging (Jafarzadeh et al. 2020; Sultana et al. 2021; Sharanyakanth and Radhakrishnan 2020). The paper aims to summarize the application of metal–organic frameworks in the food packaging sector.

Metal–organic frameworks are an extensive class of hybrid organic–inorganic supramolecules composed of metals ions linked via organic bridge ligands forming a crystalline-porous structure (Rocio-Bautista et al. 2019). Metal–organic frameworks possess a higher specific surface area than traditional porous material (Farah et al. 2012). Dynamic interactions, size, and selectivity between pores and target guest molecules can be regulated via organic and inorganic building blocks (Deng et al. 2010; Gucuyene et al. 2010). Commonly used metal ions for the fabrication of chemically stable metal–organic frameworks are aluminum, iron, zirconium, titanium, copper, and zinc (Yuan et al. 2018; Low et al. 2009; Neves et al. 2021).
Earlier, hydrothermal and solvothermal methods were used to synthesize metal–organic frameworks, but they had a drawback of long processing time. This led to the development of advanced techniques such as mechanochemical, microwave-assisted, sonochemical, electrochemical methods. Solvothermal or hydrothermal methods involve conventional electric heating in nuclear magnetic resonance tubes or vials (Lee et al. 2013). In the microwave-assisted method, the Teflon vessel is loaded with substrate components and solvent. It is then sealed and exposed to microwave radiation to generate a specific controlled temperature and a particular time. In this method, the oscillating electric field is combined with the permanent dipole moment of the molecules present in the solvent medium, causing heating (Kerner et al. 2001; Xu et al. 2006). The porous chromium trimesate (MIL-100) was the first known metal–organic framework synthesized via the microwave-assisted method (Jhung et al. 2005). In sonochemical synthesis, the solution is loaded into the horn-type Pyrex reactor attached with a sonicator bar. Sonication promotes the formation and collapsing of the bubble (known as acoustic cavitation) resulting from high pressure and temperature, ultimately leading to the fabrication of fine crystals (Stock and Biswas, 2011). In electrochemical synthesis, anodic dissolution is used as a metal ion producer which reacts with the dissolved linkers and salts present in the medium. Deposition on the cathode can be prevented by using protic solvents, but it produces hydrogen as a by-product (Mueller et al. 2006). In mechanochemical synthesis, intramolecular bonds are broken mechanically following chemical transformation (Stock and Biswas, 2011). Figure 1 represents the diagrammatic illustration of types of synthesis method of metal–organic frameworks.

Metal–organic frameworks act as adsorbents and catalysts for air purification due to their ability to remove particulate matter from the air (Decoste and Peterson 2014; Barea et al. 2014; Wang et al. 2018; Zhang et al. 2016; Chen et al. 2017). Removal of free fatty acids and peroxy compounds can be performed via cobalt, iron, and zinc-based metal–organic frameworks (Vlasova et al. 2018). Metal–organic frameworks have scope in the development of hydrogen peroxide detection sensors. In the food industry, hydrogen peroxide is widely used for sterilization of equipment and also for preservation. But exceeding the permissible limit (35% (w/w) in food package) may lead to serious health issues. This issue has encouraged the development of the iron oxide-based metal–organic framework sensor. Metal–organic frameworks can be used as a sensor; for instance, luminescent metal–organic frameworks can be used as fluorescent sensors for effective monitoring and to decrease the food safety monitoring problems (Du et al. 2021). Similarly, many other

![Fig. 1 Common methods for synthesis of metal–organic frameworks: a hydrothermal or solvothermal synthesis, b microwave-assisted synthesis, c sonochemical synthesis, d mechanochemical synthesis, and e electrochemical synthesis](image-url)
electrochemical and fluorescence metal–organic frameworks have been studied to determine chemical quality and food safety (Liu and Yin 2016). In an investigation, cellulose-based material was incorporated with MIL-125(Ti)-NH₂ (nano-metal–organic frameworks). It was observed that the mechanical performance, including tensile strength and elongation at break of the film, improved by 6.5~25.9%, and a slight increment in contact angle from 60.6° and 60.9° was also recorded. Hence, it has been concluded that the incorporation of nano-metal–organic frameworks in cellulose film can be used for the development of multifunctional film, which has application in the packaging of food (Sun et al. 2021).

The focus of this review paper is limited to the various potential roles of metal–organic frameworks in food packaging. It also highlights the challenges which need to be overcome to obtain a food packaging incorporated or made up of metal–organic frameworks with desired attributes. Moreover, efforts are being made to implement techniques such as surface modification to design metal–organic frameworks as an effective active agent.

**Metal–organic frameworks**

Widely used active agents such as zeolite have been studied seen for several years but have certain shortcomings, including high operational cost and low thermal stability (Kathuria et al. 2021; Ghazvini et al. 2021). This led to the study of metal–organic frameworks to overcome such shortcomings and improve efficiency. Metal–organic frameworks can be classified based on the structural framework, synthesis stage, the crystal structure arrangement, and stimuli (Singh et al. 2018). Based on the structural framework, metal–organic frameworks are divided into (i) flexible metal–organic frameworks: in the presence of external stimuli, reversible change of structural conformation is possible and (ii) rigid metal–organic frameworks: structural confirmation is not possible in the presence of external stimuli. Based on synthesis stages, metal–organic frameworks are categorized into three generations: (i) first-generation metal–organic frameworks: metal–organic frameworks having basic structure consisting of an organic and inorganic moiety, (ii) second-generation metal–organic frameworks: metal–organic frameworks which undergo post-synthesis surface modification, and (iii) third-generation metal–organic frameworks: metal–organic frameworks which consist of biomolecules within the framework. Based on crystal structure arrangement, metal–organic frameworks are of two types: (i) crystalline: metal–organic frameworks which have an infinite arrangement of the regular solid framework and (ii) amorphous: metal–organic frameworks, which consists of a highly disordered framework. Based on stimuli, it is classified into single stimuli: triggered by single stimulus and multi-stimuli: triggered by more than one stimuli (Cheetham et al. 2006; Perry et al. 2009; Farha et al. 2010; Bennett et al. 2014). Figure 2 represents the classification of metal–organic frameworks.

**Metal–organic frameworks for active packaging**

Active packaging is a packaging system that involves the incorporation of active agents into the packaging material to enhance the safety, quality, and shelf life of the food (Kumar et al. 2021c; Vilela et al. 2018). Active packaging preserves food as it comprises functional systems such as releasing system, absorbing system, removing system, temperature control, microbial control, and quality control (Restuccia et al. 2010; Yildirim et al. 2018). Methods of fabricating such systems include surface modification, coating, immobilizing,
or incorporating active agents onto the packaging material (Bastarrachea et al. 2015). Active agents can be natural or synthetic, but due to consumer demand and considering the environmental impact of the packaging material, the focus is shifted toward biodegradable and edible packaging material (Valdés et al. 2014, 2015; Silva-Weiss et al. 2013). Recent studies have shown that metal–organic frameworks are one of the potential active agents as it possesses oxygen scavenging, antimicrobial, moisture absorbing, and ethylene scavenging activity. Metal–organic frameworks can also serve as host molecules for controlled release of active organic molecules such as 1-Methyl Cyclopropene (1-MCP), hexanal, ethanol among others. Such host–guest systems can be deployed for active packaging applications.

**Metal–organic frameworks as oxygen scavenger or absorber**

The presence of oxygen in the package headspace leads to oxidative reactions in food, which is one of the causes of spoilage (Gaikwad et al. 2018; Singh et al. 2021a). Removal of hazardous or undesirable gas molecules can be efficiently performed via selective gas adsorption (Singh et al. 2019). Currently, porous materials such as zeolite, activated carbon, and silica are considered for gas adsorption, which works on the principle of the pressure difference between the outside and inside of the adsorbent (Davis 2002; Dąbrowski 2001; Bein et al. 2005). But demand is arising for eco-friendly, cost-effective, energy-saving, and improved efficiency. Metal–organic frameworks possess high surface area, microporous nature (diameter < 2 nm) and high pore volume, ultrahigh porosity, and about 90% of the empty space, which makes them potential candidates as a gas absorber (Férey 2008; Janiak et al. 2010; Yaghi et al. 2003; Li et al. 2009; Kitagawa et al. 2004). Hence, metal–organic frameworks play a key role in designing an active packaging system for scavenging oxygen to enhance food shelf life (He et al. 2015). Metal–organic frameworks can be flexibly designed as per the requirement due to their well-organized structure and thermal stability (Pang et al. 2012; Cavka et al. 2008; Sindoro et al. 2013). Metal–organic frameworks are usually found in powder form, but the crystalline structure is preferable for gas adsorption. In a study, covalent organic framework was loaded with dopamine which was further incorporated into the polylactic acid matrix, and the radical scavenging study suggests the antioxidant activity of the bio-nanocomposite (García et al. 2020). The three ways by which metal–organic frameworks selectively adsorb gas are adsorbent–adsorbate interaction, molecular sieving effect, and stimuli-responsive gate-opening process (He et al. 2016). Figure 3 shows the schematic representation of metal–organic frameworks as oxygen absorbers via three pathways.

**Adsorbent–adsorbate interaction**

Adsorbent–adsorbate interaction involves the affinity of the interaction between metal–organic frameworks internal surface and adsorbent; such interaction can occur due to Van der Waals forces of interaction such as hydrogen bonding, polarity, and quadruple moment (He et al. 2016). Metal–organic frameworks can possess diverse adsorption sites with varying binding energy depending on the charges and electron cloud distribution (Ghazvini et al. 2021). In an investigation, rht-type metal–organic framework PCN-61 (consists of 5,5,5‴-benzene1,3,5-triyltris(1-ethyl-2-isophthalate) linker), was capable of absorbing hydrogen molecules more effectively attributed to strong charge–quadrupole interactions (Forrest et al. 2012).

**Molecular sieving effect**

The molecular sieving effect is selective adsorption of the specific gas molecule by metal–organic frameworks depending on pore or channel size. Metal–organic frameworks consist of minute pores and gas molecules smaller than the pore size can fit into it, resulting in selective gas adsorption. For instance, a study reported that MUF-16 (MUF = Massey University Framework) was capable of selectively absorbing carbon dioxide over methane, acetylene, ethylene, ethane, propylene, and propane (Qazvini et al. 2021). Similarly, another study shows selective nitrogen adsorption via Vanadium (II) metal–organic framework from the mixture consisting of ethylene (Jaramillo et al. 2020). Li and colleagues have reported the selective absorption of oxygen and carbon dioxide over nitrogen by tetrazolate-based ligand, 2,3-di-1H-tetrazol-5-ylpyrazine having a diameter of 4.1 Å (Li et al. 2008).

**Stimuli-responsive gate-opening process**

In the stimuli-responsive gate-opening process, gas molecules enter into the pores of metal–organic framework structure when triggered by environmental factors such as temperature (Maji et al. 2004; Ghosh et al. 2008), pressure (Kitaura et al. 2004), and light irradiation (Luo et al. 2014; Lyndon et al. 2013; Heinke et al. 2014) through gate opening. In a study, diarylethene–azobenzene metal–organic framework showed distinct adsorption of different guest molecules due to the photosensitive attribute of metal–organic framework. Radial distribution function interpreted that the center of metal–organic framework is \(-\text{N} = \text{N}^+\) photosensitive and thus, has a higher adsorption affinity toward carbon dioxide (3.4 Å) over ethane (4.3 Å) and methane (4.9 Å) (Fan et al. 2017). Temperature triggered selective gas absorption was investigated for Cu(FMA) \((4,40\text{-Bpe})_{0.5}\) [FMA = fumarate; Bpe = trans-bis(4-pyridyl)].
ethylene] metal–organic frameworks. It was observed that at 77 K temperature, metal–organic frameworks are capable of adsorbing 91.8 cm³ g⁻¹ of hydrogen over argon, carbon monoxide, and nitrogen. And on increasing the temperature to 195 K, carbon dioxide adsorption over methane was observed (Chen et al. 2007).

Metal–organic frameworks as antimicrobial agent

The antimicrobial activity of active agents depends on the structure and composition of the agent as well the cell wall of the bacteria (Singh et al. 2021d; Gaikwad et al. 2019b; Mba and Nweze, 2021; Wildigg and Helmann 2021). Studies have shown that bacteria with a thick peptidoglycan layer (i.e., gram-positive bacteria) find it difficult to penetrate through the metal–organic frameworks surface. In the case of gram-negative bacteria (i.e., bacteria with thin peptidoglycan layer), higher sensitivity is observed, and thus, low minimum inhibition concentration is capable of achieving a large zone of inhibition (Karimi et al. 2020; Rojas et al. 2019; Wyszogrodzka et al. 2016; Nong et al. 2021; Shen et al. 2020). Biocidal activity of metal–organic frameworks may occur because of the release of metal ions which disrupts bacterial cell membrane integrity and/or due to the active site on the surface of metal–organic frameworks, which degrades protein and fatty acid present on the bacterial membrane. In some cases, the synergistic effect is observed when both metal ions and bioactive organic linkers participate in antimicrobial activity. Encapsulation of antimicrobial organic or inorganic guest molecules or ions in the metal–organic frameworks is another pathway to produce biocidal guest–host molecular systems (Berchel et al. 2011). In such systems, multiple molecular species or sites can participate in antimicrobial activity, such as metal ions, active linkers, and encapsulated guests (Kathuria et al. 2019; Pettinari et al. 2021). Figure 4 displays the schematic representation of metal–organic framework’s antimicrobial activity mechanism.

Antibacterial activity of metal–organic frameworks consisting of silver, cobalt, zinc, copper, and other metal ions is widely studied and has proved potency against pathogenic microbes. The presence of light has shown a synergistic effect in improving biocidal activity. In a study, it was reported that bimetallic (Zinc and Cobalt) zeolitic imidazolate framework (Zn₅₀Co₅₀-ZIF) improves antimicrobial activity by 45% in the presence of light (Ahmed et al. 2019). In another investigation, zinc-imidazolate framework-8 (ZIF-8) metal–organic frameworks have shown more than 99.99% inactivation efficiency against E. coli in the presence of solar irradiation for two hours under conditions (Li...
et al. 2019). In research, silver nanoparticles were dispersed into the HKUST-1, which was further deposited on carboxymethylated fibers (Silver nanoparticles@HKUST-1@carboxymethylated fibers) to form a composite. Antibacterial analysis showed that (Silver nanoparticles@HKUST-1@carboxymethylated fibers) samples were capable of reducing surviving Staphylococcus aureus colonies from 170 to 1 (Duan et al. 2018). Viruses such as coronavirus, human immunodeficiency virus, and the Ebola virus have increased the concern for the development of potential antiviral agents. One of the challenges is early-stage detection to avoid spreading and as well as to implement properly on-time treatment. Some recent studies have shown the use of metal–organic frameworks for designing diagnosis techniques (Wang et al. 2020; Figueira et al. 2021). Some of the antimicrobial metal–organic frameworks are mentioned in Table 1.

**Metal–organic frameworks as moisture absorber**

Even though moisture in food products is useful for the quality of foods, excess moisture in a package is unfavorable to the quality of the food product and the integrity of the package, particularly in the case of high water activity food such as fresh produce and raw meat. In those cases, including moisture absorbers in food packages is helpful (Gaikwad et al. 2019c). The common process involved in moisture absorption in food packages is physical adsorption. Here, the moisture absorption capacity is reviewed with respect to packages containing high water activity food. Due to microporous nature, various moisture stable metal–organic frameworks can absorb moisture at relative humidity such as 10% relative humidity (Xu and Yaghi 2020). In addition, metal–organic frameworks can be geometrically and chemically modified to obtain desired attributes for water absorption and water harvesting application (Llewellyn et al. 2014; Kalmuzki et al. 2018; Rieth and Dincă 2017). The metal–organic frameworks water adsorption performance depends on three factors: (i) adsorption isotherm, (ii) mass transport water, and (iii) energy transport (Liu et al. 2020). Hydrolytic stability plays a critical role in designing metal–organic frameworks for water absorption (Li et al. 2016).

The mechanism of water adsorption by metal–organic framework can occur via three pathways: chemisorption, physisorption, and capillary condensation. In chemisorption, water adsorption is due to chemical bonding in which enthalpy is high and chances of regeneration or reusage become low (Ramanayaka et al. 2019). Various metal–organic frameworks have partially saturated metal sites which are saturated by guest neutral donor ligands, and these ligands can be removed by heating under vacuum (Kalmuzki et al. 2018). Complete activation of metal–organic frameworks leads to removal of guest ligand and provides the open metal sites. The adsorption site of water may vary depending on the thermal ellipsoids. For instance, in a study, it was observed that in (Zn)MOF-74, at 24–100 °C, the water molecule was removed from the center
of the pore, and at 195 °C, the water molecule chemisorbed is removed (Dietzel et al. 2008). Physisorption involves the adsorption of a water molecule on the primary adsorption site (near-polar hydrophilic centers), leading to water cluster formation (Furukawa et al. 2014). Capillary condensation is an irreversible process, which requires the pore diameter to be larger than the critical diameter, and it is calculated using the formula,

Table 1 Metal–organic frameworks possessing an antimicrobial activity

| Type of metal–organic frameworks | Antimicrobial activity                                                                                                           | References       |
|----------------------------------|---------------------------------------------------------------------------------------------------------------------------------|------------------|
| [Ag₂(Cedcp)]ₙ and [[Ag₄(Cmdcp)₂(H₂O)]₄H₂O]ₙ | Rupturing of the bacterial cell membrane leads to cell death. *Propionibacterium acnes* ATCC6919 strain was highly sensitive to [[Ag₄(Cmdcp)₂(H₂O)]₄H₂O]ₙ and Minimum inhibition concentration was recorded as 2.51 µM | Xie et al. (2020) |
| [Ag₆(O-IPA)(H₂O)·(H₂O)] and [Ag₆(PYDC)₂(OH)] | For [Ag₆(O-IPA)(H₂O)·(H₂O)], the diameter of zone of inhibition against *Escherichia coli* and *Staphylococcus aureus* was recorded as 20 mm and 16 mm, respectively. And for [Ag₆(PYDC)₂(OH)] it was observed as 17 mm and 14 mm for *Escherichia coli* and *Staphylococcus aureus*, respectively | Lu et al. (2014) |
| Ag₂(O-IPA)(H₂O)]ₙ(H₂O)          | Minimum inhibition concentration for *Escherichia coli* was recorded as 5 ppm, and the largest diameter of zone of inhibition was 11.12 mm | Chu et al. (2020) |
| [AgL]ₙ·nH₂O                     | Sustained release and better antibacterial property against *Fusobacterium nucleatum* (ATCC 10,953, Fn), *Streptococcus mutans* (UA159), and *Porphyromonas gingivalis* (ATCC 33,277, Pg) compared to AgNO₃ was observed by [AgL]ₙ·nH₂O | Cao et al. (2020) |
| Ag-2-methylimidazole, Ag-imidazole, and Ag-benzimidazole | In samples treated with Ag-2-methylimidazole, Ag-imidazole, and Ag-benzimidazole, *Escherichia coli* population reduced from 96.2% to 10.3%, 16.4%, and 24.5%, respectively. Viable *Bacillus subtilis* decreased from 97.3% to 16.1%, 19.5%, and 35.5% in the presence of Ag-2-methylimidazole, Ag-imidazole, and Ag-benzimidazole, respectively | Seyedpour et al. (2020) |
| Co (CoSIM1), Zn (Zn-SIM1), and Ag (Ag-TAZ) | Zone of inhibition for *Anabaena species* PCC 7120 and *Synechococcus species* PCC 7942 by Co (CoSIM1), Zn (Zn-SIM1), and Ag (Ag-TAZ) was observed as 5 mm and 3 mm, 2 mm and 1 mm, and 3 mm and 1 mm, respectively | Martin et al. (2017) |
| 1,2-bis(4-pyridyl)ethylene, 1,2-bis(4-pyridyl)propane, 1,2-bis(4-pyridyl)ethane and -[Cu₂(Glu)₄(μ-L)]·x(H₂O) | Minimum bactericidal concentration for *Escherichia coli, Pseudomonas aeruginosa, Staphylococcus aureus, Klebsiella pneumonia* and *Methicillin-resistant Staphylococcus aureus* by all the copper metal–organic framework was less than 20 µg mL⁻¹ | Jo et al. (2019) |
| Cu/H₃BTC                       | For *Escherichia coli* and *Staphylococcus aureus* zone of inhibition was recorded as 16 mm and 22 mm, respectively | Shams et al. (2020) |
| C₂₅H₁₈F₄FeN₁₂ and C₂₄H₁₆C₅F₃MnN₁₂ | Least minimum inhibition concentration for C₂₅H₁₈F₄FeN₁₂ against *Escherichia coli, Staphylococcus aureus* and *Pseudomonas fluorescence* was recorded as 0.78 µg mL⁻¹. And C₂₅H₁₈C₅F₃MnN₁₂ showed minimum inhibition concentration of 0.78 µg mL⁻¹ against *Bacillus subtilis* | Zhang et al. (2014) |
| Iron trimesate                  | Loading of Azidothymidine triphosphate (AZT-TP) into metal–organic framework improved the antiviral activity by promoting the delivery of 26% of drugs into cell within 24 h, while the pure form of AZT-TP shows less than 3% of drug uptake | Agostoni et al. (2013) |
| Zeolitic imidazolate framework loaded with rifampicin | The inhibition rate of *Escherichia coli* and *S. aureus* was more than 80% by the metal–organic framework | Song et al. (2018) |
Critical diameter = \frac{4\sigma T}{T - t}

where T is critical temperature, t is adsorption temperature, and \sigma is the van der Waals diameter of the adsorbate. It has been observed that the critical diameter of water is 20.76 Å at 25 °C (Coudert et al. 2013; Abdulhalim et al. 2017; Kalmutzki et al. 2018). Figure 5 represents the diagrammatic illustration of three pathways of metal–organic frameworks as a moisture absorber.

In a study, four metal–organic frameworks were fabricated MOF-801-P, MOF-841, MOF-808, and UiO-66 with the pore volume of 0.45, 0.53, 0.84, and 0.49 cm³g⁻¹, respectively, and the water capacity for MOF-801-P, MOF-841, MOF-808, and UiO-66 was recorded as 450, 640, 735 and 535 cm³g⁻¹, respectively (Furukawa et al. 2014). In an investigation, Cu-MOF nanoparticles were incorporated into cellulose acetate through a simple solution casting method. The incorporation of 7% of Cu-MOF resulted in increasing the contact angle from 66.2° to 78.1°, suggesting an improvement in hydrophobicity. Water vapor permeability results showed a decrease from 8.86 × 10⁻⁷ g·m⁻¹·h⁻¹·Pa⁻¹ to 5.82 × 10⁻⁷ g·m⁻¹·h⁻¹·Pa⁻¹ (Chen et al. 2021). In some studies, effect of functionalization of metal–organic frameworks is also observed to improve the desired quality of metal–organic frameworks. For instance, in an investigation, UiO-67 was functionalized with –NH₂ group, and the pore volume was recorded as 0.99 and 0.64 for UiO-67 and UiO-67-(NH₂)₂, respectively. Water uptake studies for UiO-67, at P/P₀ = 0.1, 0.3 and 0.9 was recorded as 8, 15 and 293 mg g⁻¹, respectively. And for functionalized UiO-67-(NH₂)₂, water uptake was recorded as 30, 173 and 262 mg g⁻¹ at P/P₀ = 0.1, 0.3 and 0.9, respectively (Ko et al. 2015). Hence, it can be observed that metal–organic frameworks have the potential as a moisture absorber due to their high surface area and crystalline structure.

**Metal–organic frameworks as ethylene scavenger**

Fruit ripening is one of the issues which leads to food spoilage and wastage. Shelf life and maturity of the fresh produce are impacted by the headspace concentration of ethylene phytohormone, generated by produce which accelerates ripening (Hu et al. 2019). An ethylene scavenging system is an active packaging system that promotes the preservation of fresh produce and prevents spoilage by extracting ethylene from the headspace of a package (Gaikwad et al. 2020c). The action of the mechanism of metal–organic frameworks for scavenging ethylene is not explicit; however, the available data suggests it is mainly due to electrostatic interaction between positively charged metal ions and p-electron of the ethylene molecule (Awalgaonkar et al. 2020).

In an investigation, two metal–organic frameworks, Basolite C300 (is copper-based and has trimesic acid linker group) and Basolite A520 (aluminum-based and has fumaric acid linker group), were studied for ethylene scavenging activity. The absorption study showed that 250 mg of Basolite C300 could absorb 90% of ethylene while control (without absorber) and Basolite A520 absorbed only 22%. It was also reported that the presence of carbon dioxide and nitrogen reduced ethylene absorption by around 30% of Basolite C300. The highest desorption of ethylene was recorded for Basolite C300 as 7.8% within 4 h. Thus, it was concluded that Basolite C300 could be used as a scavenger to prevent spoilage and releasing agent to aid ripening (Chopra et al. 2017). In an investigation, copper terephthalate metal–organic frameworks were prepared via a solvothermal mechanism. This metal–organic framework was placed inside a 4 L container consisting of banana and avocado and placed at 16 °C. Results suggest that in 4 L of the container, 50 mg of copper terephthalate metal–organic framework can absorb 654 μL L⁻¹ of ethylene (Zhang et al. 2016). In a study, an alginate shell was incorporated with metal–organic framework comprising aluminum and trimethyl 1,3,5-benzenetricarboxylate ligands. The ethylene absorption capacity of the designed metal–organic framework was recorded as 41.0 cm³g⁻¹ metal–organic framework at 25 °C and 101.3 kPa. It was recorded that within three hours, 0.41–0.455 mg L⁻¹ ethylene per mg
aluminum metal–organic framework was released from the metal–organic framework matrix (Guan et al. 2019).

Metal–organic frameworks have their specific site for selective binding of ethylene and ethylene action inhibitor. For instance, a study observed that ethylene and 1-Methyl-cyclopropene efficiently bind to the copper site of HKUST-1 (Pnevskaya et al. 2021). However, studies have shown the potential of metal–organic frameworks as ethylene scavengers, but the dependence of its adsorption on relative humidity limits its usage (Awalgaonkar et al. 2020).

**Incorporation of metal–organic frameworks in packaging materials**

Metal–organic frameworks are highly ordered crystalline materials. The two main criteria for developing polymeric films consisting of metal–organic frameworks are selecting appropriate metal–organic framework as per the application and choosing the method to process it into a film. Metal–organic frameworks films can be classified as polycrystalline film and surface-mounted metal–organic frameworks (SURMOFs). Polycrystalline films are films with more or less randomly oriented metal–organic frameworks, and the thickness of the film depends on the size of metal–organic framework particles. SURMOF consists of perfectly oriented metal–organic frameworks with smooth surfaces, and the thickness of the film lies in nanometers (Betard et al. 2012).

The three ways to fabricate metal–organic framework active films include in situ interweaving, post-synthetic polymerization, and solvent-free hot-pressing. In situ interweaving involves electrochemical weaving of isolated metal–organic framework on the substrate using conducting polymers. Photoinduced post-synthetic polymerization consists of two steps; firstly, functional groups are used to modify organic ligand covalently, and then organic monomers are grafted on metal–organic frameworks via graft polymerization. The solvent-free hot-pressing method involves two stages; ligands or metal ions are chemically linked to the substrate with functional groups and metal sites on the surface. And then this leads to the growth of metal–organic framework crystals on the surface and nucleation (Ma et al. 2019). Self-assembled monolayers can be used as an interface for the incorporation of metal–organic framework for preparing the composite film, but it is not a practical method. Therefore, two techniques are employed: aged precursor solutions consisting of metal and ligands are used to immerse self-assembled monolayers, and the second is via liquid epitaxial layer-by-layer approach (Bradshaw et al. 2012). Liquid phase epitaxial is a method that involves layer-by-layer adsorption to the surface and alternative immersion of the substrate in positively charged solution and then in negatively charged solution (Decher 1997). Langmuir–Blodgett layer-by-layer deposition is a method that involves the transferring of metal–organic framework layers from one after another onto a substrate (silicon), including intermediate rinsing (Kitaura et al. 2003).

Hence, it can be stated that there are various methods for the fabrication of metal–organic framework films. However, there are still some challenges limiting its commercialization which can be overcome with advancements in technology. For instance, in a study, a metal–organic framework embedded film was prepared at room temperature within one-two hours with desired attributes via metal-hydroxide-nanostrand-assisted confinement technique, in which solution of metal-hydroxide nanostrands was filtered, and the functional components are dispersed on porous matrix and further which is peeled off (Mao et al. 2014).

**Food packaging applications**

The incorporation of metal–organic frameworks into packaging materials is investigated in several studies to prevent food spoilage by absorbing moisture, preventing microbial deterioration, and delaying fruit ripening by controlling ethylene (Sharnayakanth et al. 2020). Active agent metal–organic frameworks can be incorporated into packaging in three ways: impregnation into packaging matrix, sachets, and coating (Fig. 6). Table 2 represents metal–organic frameworks in food packaging applications.

Kohsari and colleagues developed chitosan polyethylene oxide nanofibrous mats incorporated with zinc-imidazolate framework-8 nanoparticles. The antibacterial study revealed 100% inhibition of *S. aureus* and *E.coli* for chitosan polyethylene oxide nanofibrous mats consisting of 3% of zinc-imidazolate framework-8 nanoparticles. The highest improvement in tensile strength (22.78 MPa) was recorded by chitosan polyethylene oxide nanofibrous mats comprised of 10% of zinc-imidazolate framework-8 nanoparticles (Kohsari et al. 2020). In another investigation, ferric ion-doped hollow metal–organic frameworks were loaded with capsaicin and fabricated into gelatin and chitosan packaging film (Cap-FeIII-HMOF-5). Apple cubes were coated with the designed coating and observed for five days, among which 8% of capsaicin showed no bacterial spoilage and minor oxidation on the fifth day of the experiment. Water vapor permeability of the film improved from 1.236 (control) to 1.794 g·10¹⁰ (s·m·Pa)⁻¹ (8% Cap-FeIII-HMOF-5) (Zhao et al. 2020). In a study, allyl isothiocyanate (natural antimicrobial compound) was incorporated into three metal–organic frameworks: HKUST-1, MOF-74(Zinc), and RPM6-Zinc. At a relative humidity of 30–35%, metal–organic frameworks were able to retain the allyl isothiocyanate and released 70–96% at a high relative humidity of 95–100%. This can
be used to develop food packaging to prevent microbial contamination (Lashkari et al. 2017). In an investigation, poly(L-lactic acid) was loaded with 15% zinc-imidazolate framework-8 metal–organic framework to develop active packaging film. As per the migration study, migration of zinc ions in low and high alcoholic stimulants was recorded as 166 mg L\(^{-1}\) and for aqueous and acidic food simulants as 354 mg L\(^{-1}\). Since the migration percentage was higher than acceptable, it cannot be considered for direct food contact (Kathuria et al. 2021).

Metal–organic frameworks can also be used to reduce the film's water vapor transmission rate; for instance, in a study, Zr\(_6\)O\(_4\)(OH)\(_4\)(fumarate)\(_8\) was incorporated into cyclic olefin copolymer, and the water vapor transmissions rate study revealed a tenfold increase in the film containing metal–organic frameworks (Bae et al. 2016). Thus, researchers have reported the promising potential of metal–organic frameworks as an active agent to be impregnated into the packaging matrix to develop active, intelligent, smart materials for developing sustainable product-package systems for reducing food waste and greenhouse gas emissions.

**Perspective**

Metal–organic frameworks have vast applications potential because of their tailorability, diverse structural and compositional manipulation. However, several challenges exist which need to be addressed for their mass-scale food packaging applications. Some of them are mentioned below:

Although complications in the large-scale production of metal–organic frameworks (Kong and Li 2021) exist, researchers have reportedly produced metal–organic frameworks by extrusion processing (Casaban et al. 2021).

Separation of gas molecules having similarities in size is difficult via metal–organic frameworks (Hendon et al. 2017).

Fabrication of metal–organic frameworks is an expensive method (Julien et al. 2017). However, new fabrication methodologies such as extrusion have been reported, which indicates a promising future.

The capacity of metal–organic frameworks is low, which need to be modified (Vikrant et al. 2017).

Recycling of metal–organic frameworks is not an easy process (Kumar et al. 2019).

Toxicity of the metal–organic frameworks due to metal ions and organic ligands functional groups (Ouyang et al. 2018; Barea et al. 2014; Sajid, 2016; Jung et al. 2010).

Recycling and toxicity can be addressed by using naturally occurring biomolecules as ligands and environmentally benign transition metal or non-toxic metal ions such as alkali or alkaline earth metals.

Continuous scientific advances and understanding in the field of microporous and mesoporous materials have increased the possibility of commercial utilization of metal–organic frameworks in food packaging applications. Further modification or the tailored design of metal–organic frameworks can help in improving their functional performance. Such as, an efficient synthesis of metal–organic frameworks can be attained by reducing energy input, opting for safe and less costly building units, and implementing continuous processes (Kong and Li, 2021). The reviewed literature suggests the applications of metal–organic frameworks in the packaging of fruits and vegetables during transportation and storage to scavenge ethylene which delays the ripening and maintains the freshness of the food. Metal–organic frameworks also have scope in the packaging of meat-based products to prevent lipid oxidation and microbial contaminations, which are the major cause of
Table 2  Metal–organic frameworks for food packaging application

| Metal–organic frameworks                                      | Active compound | Synthesis method                  | Food                      | Outcomes                                                                 | References         |
|---------------------------------------------------------------|-----------------|-----------------------------------|---------------------------|---------------------------------------------------------------------------|--------------------|
| Cyclodextrin-based metal–organic framework                    | Hexanal         | Vapour diffusion method           | Mango                     | Shelf life was extended to 15 days                                        | Nagarajan et al. (2021) |
| Single-walled nickel–organic framework                        | –               |                                   | Banana                    | Banana placed in 1-L jar consisting of metal–organic framework showed no sign of spoilage till 30th day while in control dark spot was observed on 9th day of storage | Li et al. (2021)   |
| MIL-101@CMFP and UIO-66@CMFP                                  | Curcumin        | –                                 | Pitaya                    | Curcumin-loaded nano-metal–organic framework extended the shelf life of pitaya to 6 days while control showed the sign of spoilage on 2nd day of storage | Huang et al. (2021) |
| Electrospun pullulan/polyvinyl alcohol nanofibers incorporated with porphyrin metal–organic framework | Thymol          | –                                 | Fresh grapes and strawberries | Grapes wrapped in metal–organic framework showed no spoilage for 7 days while control got rotten on the 7th day. Strawberries remain fresh for 7 days when wrapped with metal–organic framework while control showed mold growths | Min et al. (2021)  |
| Silver-based metal–organic framework                          | Chitosan        | One-pot synthesis method          | Pitaya                    | Spraying metal–organic framework solution on pitaya maintained its freshness for 14 days while control spoiled on the 7th day due to mold growth | Zhang et al. (2022) |
| Copper terephthalate metal–organic framework                  | Solvothermal     |                                   | Bananas and Avocados      | The shelf life of bananas and avocados was extended                        | Zhang et al. (2016) |
meat spoilage. Oxygen and moisture absorbing attributes of the packaging make it a good candidate for packaging crispy food products and maintaining the quality of food by preventing it from becoming soggy. Hence, food packaging involving metal–organic frameworks as an active agent has a promising potential to maintain food safety, quality and extend its shelf life.

Conclusion

To achieve food safety, it is necessary to detect, control, and remove the hazards and risks while the food reaches from the farm to the consumer's plate. Metal–organic frameworks act as potential agents due to their unique chemical and physical attributes. In this review, we have outlined various applications of metal–organic frameworks in food packaging. The role of metal–organic frameworks such as antimicrobial agent, antioxidant agent, oxygen scavenger, ethylene scavenger, and moisture absorber is discussed. The reviewed literature showed that the biocompatibility and nonreactive behavior of the metal–organic frameworks had increased the demand in the food packaging field. There are certain shortcomings such as high fabrication cost, recycling issue, low capacity, and inefficient separation of gas molecules, limiting the commercialization of metal–organic frameworks application in food packaging. Overcoming these challenges would help in the fabrication of efficient packaging material impregnated with metal–organic frameworks to maintain food safety, quality and extend its shelf life.

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Authors contribution The authors conceptualized the study design jointly. AS searched for and resolved conflicts, charted the data, and wrote the first draft. AK and KKG led the analysis and incorporated critical feedback from all authors.

Declarations

Conflict of interest The authors declare that they have no conflict of interest.

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