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REVIEW

Ethylene scavengers for active packaging of fresh food produce

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Abstract
Many fruits and vegetables are sensitive to ethylene, which upon prolonged exposure induces the deterioration of food quality, such as change in taste, odour and colour, or microbial growth. Therefore, ethylene scavengers in packages can be used to limit ethylene accumulation. Ethylene scavengers extend the shelf life and retain the original food quality. Here, we review ethylene scavenging systems such as potassium carbonate, palladium, natural clays, titanium dioxide-based, electron-deficient dienes and trienes. Ethylene scavenging is done by chemical reactions and physical adsorption. We then discuss the applications and benefits of ethylene scavengers in packages. The efficiency of ethylene scavengers is improved using atmospheric packaging tools.

Keywords Ethylene scavenger · Fresh produce · Food packaging · Modified atmosphere · Active packaging · Shelf life

Introduction

Packaging is a global industry of high diversity. There is a growing scientific interest on packaging that come into contact with food products. As a result of the growing consumer interest in the consumption of fresh produce with extended shelf life and maintained quality, producers have to provide advance and safe packaging. Packaging technology is specifically crucial for fresh produce as quality can only be maintained after harvest and not enhanced. When boosted, food packaging increases the suitability, safety and quality of food products for customers, whereas reducing the need for preservatives, food waste and the rate of food poisoning (Robertson 2012; Ahn et al. 2016; Gaikwad et al. 2019a; Gaikwad et al. 2020). This can produce substantial cost savings and economic advantages for food retailers and food industries (Vilela et al. 2018; Brody et al. 2001).

Active packaging is a technology, in which packaging, product and environment interrelate. These are the systems, which actively vary the conditions of the packed food, cause the addition of its sustainability and hence shelf life and guarantee while maintaining its quality (Choi et al. 2016; Singh et al. 2016a; Gaikwad et al. 2019b). In divergence to the traditional packaging materials, active packaging causes prolonging the shelf life of food and maintaining its quality during reactions with the intimate atmosphere and the product (Vilela et al. 2018; Singh et al. 2019a, b). Thus, active packaging technology should be considered an excellent way in the area of food packaging (Singh et al. 2019a, b).

Ethylene (C_2H_4) is a pure unsaturated hydrocarbon found in nature. It is a volatile compound of enormous significance as a plant hormone. This hormone formed by higher plants activates and hence controls physiological mechanisms, development, regulating growth, ripening and senescence aspects of plants (Zhu et al. 2019; Gaikwad and Lee 2017a). Ethylene produces physiological responses, for example geotropism, ripening, senescence, dormancy and flowering (Singh et al. 2018a, b, c, d). The low concentration edge required for triggering physiological activities validates that reducing ethylene in a closed atmosphere can help the postharvest durability of fresh produce (Bailén et al. 2006; Gaikwad et al. 2017b), apart from these postharvest losses and quality deterioration of fruits and vegetables mostly caused

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by the ripening process induced by ethylene and contamination due to micro-organisms (Singh et al. 2016b). Active packaging prevents the adverse effects of ethylene gas and prevents microbial growth. Ethylene scavenger is required to extend the shelf life of fresh produce as presented in Fig. 1, and it is an excellent alternative to the use of chemical usages and disinfectants (Martínez-Romero et al. 2007; Dainelli et al. 2008).

An effective way to regulate ethylene production inside the package is to use of an ethylene scavenger. Ethylene scavenger absorbs ethylene produced by fresh produce to control postharvest losses and quality deterioration (Mujtaba et al. 2014; Gaikwad and Ko 2015; Li et al. 2011). The standard packaging form of ethylene scavengers is sachets, films and corrugated box which generally employed to maintain ethylene gas concentration inside the package. Ethylene scavenging materials typically contained inside small sachets for fresh produce packaging application that is added to the package to control the excessive ethylene from the fruits and vegetables which generates in the package during storage (Brody et al. 2001). Scavenger reacts with ethylene via physical or chemical adsorption process. The approaches for the ethylene regulation can be categorized into three main types: firstly, reduction in ethylene (via modified atmospheric packaging through swapping the different gases in the headspace); secondly, use of perforated packaging material (by using microperforated packaging materials to permeate the gases to inside and outside of package); and thirdly, ethylene removal (by using ethylene scavenger). Ethylene scavengers (water absorption is by means of a chemical reaction between two materials) or ethylene absorbers (materials who physically absorb and hold ethylene molecule) are starting to be used by supermarket chains, for example Tesco and M&S for fresh fruit and vegetable packaging applications to decrease spoilage and increase shelf life (Boonruang et al. 2012; Gaikwad et al. 2017b; Singh et al. 2018b).

Despite the fact that there has been significant attention and advance in the field of active packaging for food packaging applications (Yildirim et al. 2018; Gaikwad et al. 2018b), relatively very little consideration has been paid to ethylene scavenger. Therefore, this review aims to offer an overview of ethylene scavengers used for active fruits and vegetable packaging applications. We first discuss the significant types of ethylene scavenging materials categorized by their nature, their ethylene scavenging mechanism, trends in ethylene scavenging packaging; then, we provide an overview of fresh produce applications, which is the future perspective for the ethylene scavenger.

Ethylene scavenging mechanisms

Ethylene scavengers are effective in eliminating ethylene concentrations in the package (Ozdemir and Floros 2004). The double bond present in gaseous ethylene makes it is a very reactive compound that can be changed or degraded in numerous ways (Chowdhury et al. 2017). This generates a diversity of opportunities for commercial methodologies for the elimination of gaseous ethylene. The main considerations when evolving profitable technologies are not only the technical aspects, e.g. scavenging capacity and rate, mechanisms, derivatives, prospective interactions or reactions with the other active packaging technologies, and fresh produce, but also regulation and marketing issues, e.g. food safety, cost, and consumer acceptance. Ethylene scavenging can be done by chemical or physical methods (Yildirim et al.

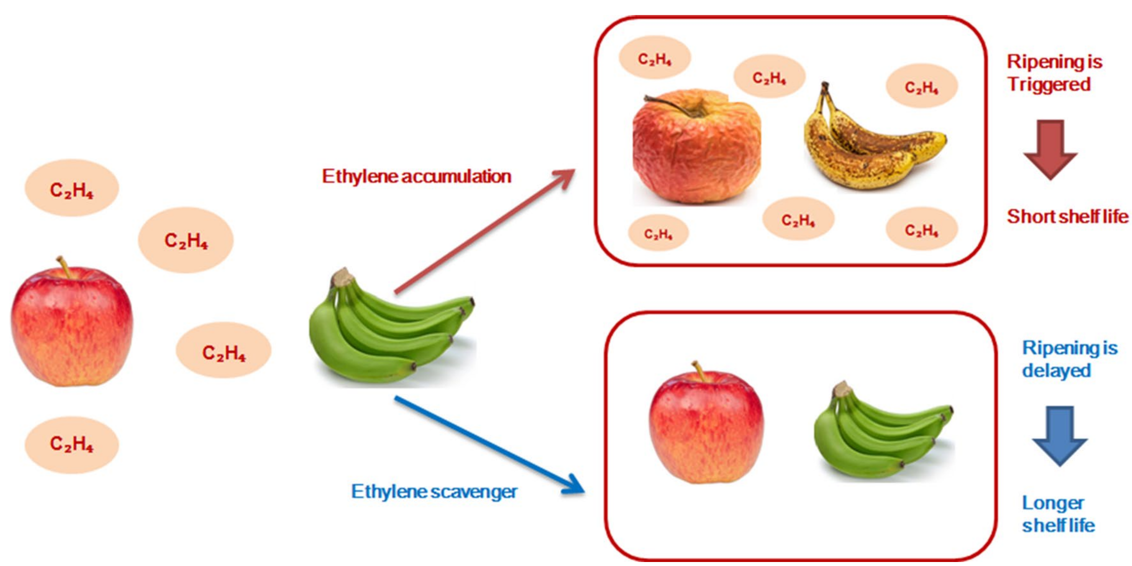


Fig. 1 Effects of postharvest ethylene accumulation and ethylene scavenger on the ripening and shelf life of fresh fruits

2018). These methods exploit the capacity of some materials or treatment to oxidize, decompose or adsorb ethylene gas, employing different mechanisms. Effective systems use potassium permanganate ($KMnO_4$) immobilized on an inert mineral substrate, for example alumina or silica gel. The alumina functions mainly as the absorptive surface to hold the molecules of ethylene gas and is a carrier for the permanganate. KM_nO_4 is a wide-spectrum oxidizing agent that reacts with ethylene along with other contaminant gases. When it reacts by oxidizing ethylene to ethylene glycol, a visible colour change takes place. As shown in Fig. 2, ethylene is initially oxidized to acetaldehyde, which in turn is oxidized to acetic acid, and acetic acid is further oxidized to carbon dioxide and water. The typical ethylene scavenging reaction for potassium permanganate is as follows:

$$3CH_2 + 2KM_nO_4 + H_2O \rightarrow 2MnO_2 + 3CH_3CHO + 2KOH \quad (1)$$

$$3CH_3CHO + 2KM_nO_4 + H_2O \rightarrow 3CH_3COOH + 2MnO_2 + 2KOH \quad (2)$$

$$3CH_3COOH + 8KM_nO_4 \rightarrow 6CO_2 + 8MnO_2 + 8KOH + 2H_2O \quad (3)$$

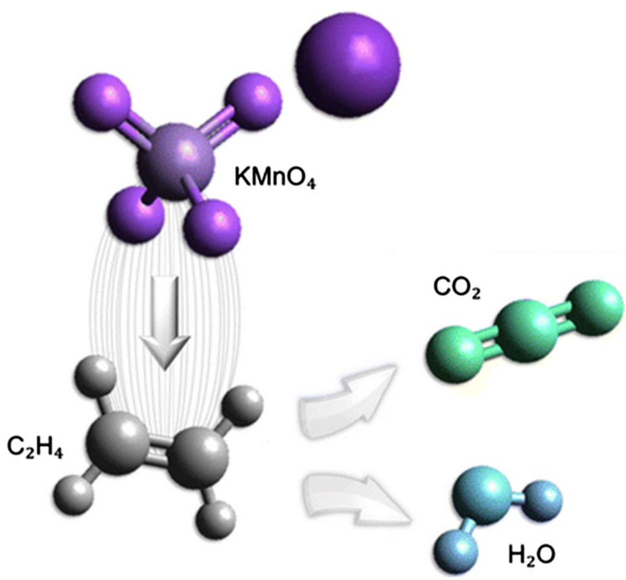


Fig. 2 Ethylene oxidation reaction by potassium permanganate-based scavenger Modified from Álvarez-Hernández et al. (2018)

Relating Eqs. 1–3, we get

$$3CH_2CH_2 + 12KM_nO_4 \rightarrow 12MnO_2 + 12KOH + 6CO_2$$

Physical adsorption of ethylene is caused by van der Waals force among the molecules of the adsorbent and the adsorbate (Ponec et al. 1974). Solid adsorbents through mesopores can adsorb distinct and consecutive layers of adsorbate, whereas those with micropores have the size of the pores of 0.6–0.3 mm filled with the adsorbate. Solid adsorbents develop the selectivity to the adsorbate after the former go through particular alkaline treatments, like reacting under a gas stream or with definite agents. The standard physical adsorbents are activated carbon, carbon fibre, silica gel and zeolite (Álvarez-Hernández et al. 2018).

Ethylene scavenging systems

In principle, ethylene scavenging systems comprise either inclusion of a small sachet containing an appropriate scavenging agent in the packaging or incorporation of an ethylene scavenger in the packaging material structure. The sachet material should be highly permeable to gaseous ethylene, allowing diffusion through it (Yildirim et al. 2018; Gaikwad et al. 2017a). Effective ethylene scavenger can be further divided into two main categories: ethylene absorbers and scavengers; absorbers are those materials who physically absorb and hold ethylene molecule from the surrounding environment, and on the other hand, ethylene scavenger, where water absorption is by means of a chemical reaction between two materials (Vilela et al. 2018). The latter can be applied in the form of sachets and films and are typically placed in fresh produce package. Price, safety, and the ethylene scavenging capacity restrict the range of candidate materials for fresh produce packaging applications. Some potential ethylene scavenging materials by their nature for fresh produce packaging applications are classified in Table 1. Despite the fact that most commercial ethylene scavengers are made from potassium permanganate for high ethylene activity fresh produce, the fresh produce industry has become progressively interested in the development and application of novel ethylene scavenging materials in the plastic film form packages.

Table 1 Ethylene scavenging materials for food packaging applications

Type	Ethylene scavenging materials
Natural clays	Zeolite, halloysite nanotube, Japanese Oya stone, cristobalite, bentonite, coral, ceramics
Regenerable sorbents	Propylene glycol, hexylene glycol, squalene, phenymethylsilicone, polyethylene, polystyrene
Catalytic oxidizers	Potassium permanganate, potassium dichromate, iodine pentoxide and silver nitrate, palladium
Electron-deficient dienes or trienes	Benzene, pyridines, diazines triazines, tetrazines (*Having electron-withdrawing substitutes*)
Other	Activated charcoal, crystalline aluminosilicates, kieselguhr, silica gel, aluminium oxide

Potassium permanganate-based systems

Over the years, the most recognized, economical and commonly used ethylene scavenging system has been those based on potassium permanganate (KMnO4), a reliable agent that chemically scavenges C2H4 by an oxidation process (Ozdemir and Floros 2004; Yam 2010). To expand the surface area of absorption, $KMnO_4$ reinforced on inert matrices, for example silica gel or alumina, which oxidizes gaseous ethylene with a colour change from purple to brown. Spricigo et al. (2017) developed a nanostructured ethylene scavenging system based on silica and alumina nanoparticles impregnated with $KMnO_4$ that took advantage of this colour change to indicate ethylene scavenge. Author claims that developed inorganic compound has a high prospective as ethylene scavenging sachets during storage of tomatoes under 5–6 °C storage conditions. However, due to high toxicity and inadequate long-term effectiveness in high moisture condition, $KMnO_4$ cannot be used in direct contact with foodstuffs (Yildirim et al. 2018). Usually, such scavengers contain about 4–6% $KMnO_4$ on an inert substrate, for example perlite, alumina, silica gel, vermiculite and activated carbon or Celite. The scavenging capacity and uses of such scavengers can be influenced by substrate surface area and the content of $KMnO_4$. Constructions differ in density and surface area of the substrate and the loading of KMnO4 (Zagory 1995).

At present, available scavengers in the market have an ethylene scavenging capacity ranging from 3 to 6.5 L kg^{-1} (Scully and Horsham 2007). Moreover, there are some commercial KMnO4-based scavengers, for example Chemisorbant (Purafil, Inc., Doraville GA, USA), MM-1000 MULTI MIX® MEDIA (Circul-Aire Inc., Montreal, Canada), Bi-On® SORB (Bioconservacion S.A., Barcelona, Spain) and SofnofilTM (Molecular Products Limited, Essex, UK). $KMnO_4$-based ethylene scavengers are available in the form of sachets/bags, tube filters, blankets, labels and films, with the most commonly used form being sachets as they are appropriate for individual packaging applications (Janjarasskul and Suppakul 2018). The list of commercially available ethylene scavengers for fresh produce packaging applications is presented in Table 2.

Clay-based systems

Several clays have been stated to have ethylene adsorbing capacity. Clays are hydrous covered aluminosilicates composed of two layers, including tetrahedral and octahedral layers (Tas et al. 2017). Tetrahedral layers consist of areas of Si^{4+}, but Al^{3+} is also very common, although the octahedral layers typically consist of Mg^{2+} or Al^{3+}, despite the fact that Fe^{2+}, Ni^{2+}, Li^{+}, Fe^{3+}, Cr^{3+} may also exist (Bhattacharyya and Gupta 2008). Ethylene is possibly removed by physical adsorption on materials with active surfaces, for example activated carbon, zeolites and some clays (e.g. pumice, cristobalite and clinoptilolite). These clays can be contained into an ethylene-permeable sachet, or fine particles of such clays can be incorporated into the packaging film via extrusion process (e.g. plastic films) (Gaikwad et al. 2018a).

Ethylene elimination using zeolite as an adsorbent has received significant attention in both industry and agriculture applications. Hence, zeolite-based ethylene scavengers are worthy material for commercial applications (Yam 2010). It is stated that the beneficial properties of the hollow are thought to exist in the large zeolite interior. The most distinctive property of zeolites is their porous with three-dimensional structure with cation interchange, adsorption and molecular separating properties. Thus, zeolites have been used in numerous industrial and agricultural applications, as well as an ethylene scavenging material integrated into packaging material such as film. There are numerous reports that incorporation of zeolites allows high gas permeability of packaging materials through their crystalline porous three-dimensional structure (Dirim et al. 2004). Recently, Coloma et al. (2014) developed zeolite-based ethylene scavenger with the use of montmorillonite and further incorporated with low-density polyethylene which showed after 50 h, elimination of 37% of ethylene present in package headspace was achieved by using 10% of the scavenger.

Some other natural clays having a porous structure such as halloysite nanotubes, montmorillonite, Cloisite, and Japanese Oya have increased much consideration as ethylene scavengers for fresh produce active packaging applications. Halloysite nanotubes (HNTs) are "green" materials mined from natural deposits (Gaikwad et al. 2018a; Tas et al. 2017). HNTs have high phase ratio that permits them to be used as nanocarriers and can be well dispersed in the polymer structure, resulting in the discharge of the active agent in nanocomposite (Yuan et al. 2015). Due to safe for food packaging applications, encapsulation capability, and suitability for integration into polymers as a nanocomposite material, HNTs are an ideal functional material for fresh produce packaging applications. Typical structure of HNTs is shown in Fig. 3 (Chowdhury et al. 2017). In recent studies, HNTs were explored for various applications, including nanoscale containers for functional compounds, adsorbents and polymer fillers (Szpilska et al. 2015). Tas et al. (2017) developed an ethylene-absorbing packaging film by using HNTs and low-density polyethylene for fresh produce packaging application. Gaikwad et al. (2018a) investigated alkali-treated HNTs as an ethylene scavenger. Results showed that within 24 h, 1 g of alkali-treated HNTs scavenged 49 µL ethylene gas from the package tested. HNTs are generally recognized as safe (GRAS) for food packaging applications by the US FDA (Lee et al. 2017). HNTs can be used as a substitute for traditional chemical-based ethylene scavengers

Table 2 Commercially available ethylene scavengers for fresh produce active packaging applications

Manufacturer	Commercial name	Active material	Available form
Mitsubishi Gas Chemical Co. Ltd., Japan	SendoMate	Activated carbon with a metal catalyst	Sachet
Deltatrak Inc., USA	Air repair	Potassium permanganate	Sachet
Biopac Pty Ltd., Australia	BIOPAC	Porous material mixed with potassium permanganate	Sachet
BioXTEND Co., USA	BioX® 4.0	Alumina-mixed potassium permanganate	Sachet
Ethylene Control, Inc., USA	Super Fresh Media	Natural zeolite with potassium permanganate	Sachet
AgraCo Technologies International, LLC, USA	Extend-A-Life™	Zeolite coated with potassium permanganate	Sachet
Retarder S.R.L, Italy	Retarder®	A mix of clays and potassium permanganate	Sachet
Befresh Technology, Spain	BEfresh	Natural clays impregnated with potassium permanganate	Sachet
Prodew Inc., USA	Prodew	Potassium permanganate granules	Sachet
Marathon products, USA	Ethylene filter products	Zeolite	Sachets
Sensitech Inc., USA	Ryan®	Mixture of natural clays and potassium permanganate	Sachet
Sekisui Jushi Corp., Japan	Neupalon	Activated carbon with a metal catalyst	Sachets
Purafil, Inc., Doraville GA, USA	Purafil	Activated alumina impregnated with potassium permanganate	Sachets
Desiccare, USA	Ethylene eliminationPack	Zeolite	Sachets
Molina de Segura, Spain	KEEPCOOL	Sepiolite mixed with potassium permanganate and activated carbon	Sachet
KeepFresh Technologies, Malaga WA, Australia	KEEPFRESH	Natural zeolite impregnated with potassium permanganate	Sachet/sheet
Greenkeeper Iberia, Spain	GKZ4	Zeolite loaded with potassium permanganate	Sachet/sheet
Odja Shoji Co. Ltd., Japan	BO film	Crysburite ceramics	Polymeric film
E-I-A Warenhandels GmbH, Austria	Profresh	Minerals	Polymeric film
Nippon Container corporation, Japan	FAIN		Polymeric film
OhE Chemicals, Japan	Crisper SL	–	Polymeric film
Evert-Fresh Corporation Ltd., USA	Evert-Fresh	Zeolite	Bags
Cho Yang Heung San Co. Ltd., South Korea	Orega bags	Minerals	Bags
Grofit Plastics, Israel	Biofresh	–	Bag (Zipper)
Honshu Paper, Japan	Hatofresh System	Activated carbon with bromine	Paper bags/corrugated box
Miatech, Inc., USA	Eris filter	Potassium permanganate granules	Sheet
Molecular Products Limited, UK	Ethysorb®	Activated alumina with potassium permanganate	Bulk beads/tube/blanket
Bry-Air (Asia) Pvt Ltd., India	BRYSORB™ 508	Activated alumina with potassium permanganate	Granules
Dennis Green Ltd., USA	Mrs Green extra life	Potassium permanganate	Cartridge for refrigeration
Isolcell Spa, Italy	PURETHYL	Activated alumina granules with potassium permanganate	Machine

in applications where cost is a concern. Their economical and high performance ease the industrialization of HNTs polymer nanocomposites.

Oya stone is found in Japan and has ethylene scavenging capacity. This stone is mined from the Oya cave-in area of Tochigi Prefecture in Japan. To increase ethylene adsorbing capacity, Oya stone is first finely ground with a slight amount of metal oxide. The obtained mixture is then presses and heated to 200–9000 °C, and then, further it oxidizes under ozone or electromagnetic radiation (Urushizaki 1987). The Oya stone has been used to store fresh horticulture produce and is reputed to confer added storage life.

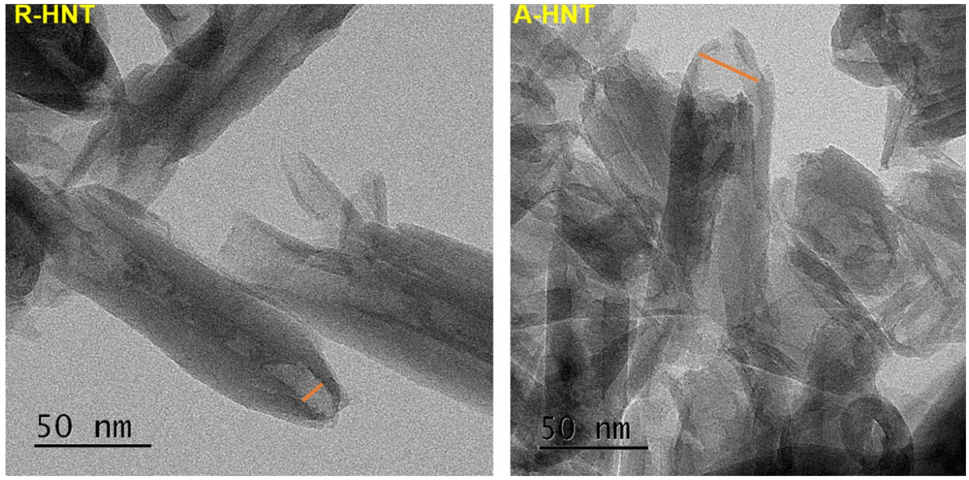


Fig. 3 Transmission electron microscope (TEM) images of raw and alkali-treated halloysite nanotubes Adapted and modified from Gaikwad et al. (2018a, b, c)

Activated carbon-based systems

Activated carbons are non-crystalline porous with structure, and it is a form of carbon acquired by pyrolysis of carbonaceous substance (Sneddon et al. 2014). The initiation step of carbon is supported out to produce more pores and alter their volume, arrangement and size, and it can be done via physical and chemical methods. The maximum number of commercial grades of activated carbons typically retain a pore volume in between 10 and 25 Å in diameter and its surface area in between 300 and 4000 m^2 $g^{-}1$, but very few of them can extend the surface areas up to 5000 m^2 $g^{-}1$ (Gaikwad et al. 2018a). Activated carbons can be in the form of granular, powdered or fibre, presenting the most ideal granular form because of its more natural regeneration and adaptability. Besides, it has been reported that the best ethylene adsorption capacity of activated carbons is carried out by using granular form compared with powder form and fibre forms (Martínez-Romero et al. 2007). Bailén et al. (2006) assessed the effect of modified atmosphere packaging by using polypropylene bags having 20 µm thickness with sachets form of ethylene scavenger containing 5 g granular active carbon (specific surface area of 226 m^2 $g^{-}1$) on tomato quality during postharvest storage at 8 °C and 90% RH. The results showed that granular activated carbon delayed the variations in colour, firmness and weight in tomato fruits, whereas ethylene levels significantly inside packages up to 14 days. Activated carbon can be merged with other compounds, for example $KMnO_4$, to increase its adsorption capacity. However, there is a limited research study about the ethylene scavenging capacity of activated carbon and $KMnO_4$, although its use as ethylene scrubber is widely mentioned in the past studies (Brody et al. 2001). Activated carbon has advantages, for example hydrophobic nature, high surface area and production cost being relatively cheap.

Palladium-based systems

Johnson Matthey researcher firstly studied the use of new palladium-promoted material with a significant ethylene adsorption capacity at room temperature. Ilkenhans et al. (2007) developed palladium-based scavenger with significant ethylene adsorption capacity. The developed material effectively scavenged the ethylene produced by climacteric fruit. Results showed that the fruits have delayed the ripening process. Further, Terry et al. (2007) developed palladium-promoted powder-based scavenger that has 4162 µL g^{-1} material ethylene adsorption capacity at 20 °C. Results showed that the efficiency of palladium-promoted scavenger was far superior to $KMnO_4$ when utilized in small quality and particularly at high relative humidity. Martìnez-Romero et al. (2009) stated that the efficiency of activated carbon 1% palladium to remove the accumulated ethylene in the package was approximately 60% over time. Bailén et al. (2006) reported that the use of 1% palladium with activated carbon was more effective than single activated carbon in preserving the quality of tomato fruits in modified atmospheric packaging (MAP) system. Bailen et al. (2013) showed that palladium-altered activated carbon was useful for scavenging gaseous ethylene. Additional try of using palladium-doping catalysts, for example titanium dioxide (TiO_2) and zeolite (clay), has been proficient for degradation of ethylene, polyphenol and dyes. However, the use of palladium-doping zeolite in delaying the shelf life of banana thru postharvest is barely studied.

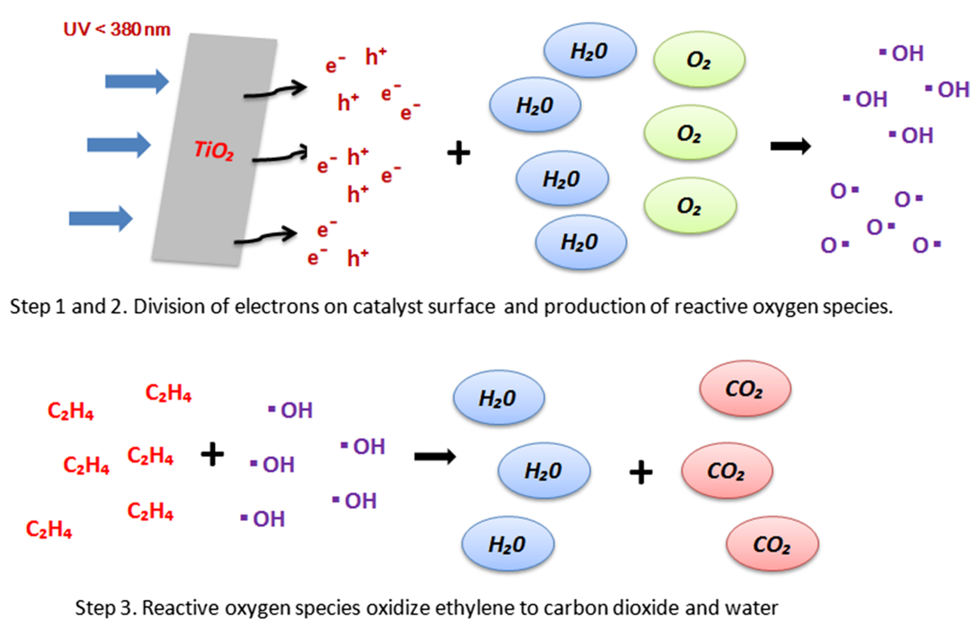
Titanium dioxide-based systems

The photocatalytic oxidation of gaseous ethylene includes exposure to ultraviolet (UV) radiation and the use of a catalyst, for example titanium dioxide (TiO_2). At the surface of the catalyst, illumination with UV radiation generates reactive oxygen species (ROS), which further oxidize ethylene into carbon dioxide and water. In contrast, irradiation with significant shortwave vacuum UV radiation inspires photochemical oxidation processes, leading to the creation of ROS in the gaseous phase by decomposing oxygen and molecules of water, and these reactive species oxidize the ethylene. One of the favourable solutions for ethylene elimination is a nanotitanium dioxide-based photocatalytic system. The mechanism of scavenging is reactive oxygen species which are produced on the TiO_2 surface following exposure to UV light, thus further oxidizing ethylene into carbon dioxide and water (Fig. 4). The titanium dioxide-based scavenging system does not need high temperature or pressure for scavenging, and it is less energy demanding as compared to thermal catalytic oxidation. Such scavenging system does not need frequent replacements and produces nominal waste that is green technology. Yang et al. (2010) developed polyethylene blended with nano-Ag, TiO_2 and kaolin clay for the preservation of fresh strawberries stored at 4 °C for 12 d. Results showed that functional polyethylene with nano-TiO_2 preserved physicochemical and physiological qualities of strawberry fruits that are better than the control sample. In recent years, several composite films containing TiO_2 to eliminate gaseous ethylene at altered UV light intensity ranging from 42 to 2.5 mW cm^{-2} have been reported. Tanaka et al. (2006) developed an adsorbent-embedded TiO_2 composite film by sol–gel technique. Maneerat and Hayata (2008) used a polypropylene-based film and coated with TiO_2 as a functional ethylene scavenging packaging material. A chitosan and TiO_2 nanocomposite films were also cast to extend the shelf life of tomato fruit (Kaewklin et al. 2018). Further, Wang et al. (2010) confirmed that a nanopackaging system with silver and TiO_2 (with a hot-air treatment) was very effective in improving mould control and ethylene generation in Chinese bayberry fruits. TiO_2 nanorods and tin oxide nanoparticles are also utilized to detect the discharge of highly volatile organic compounds. Furthermore, tungsten oxide and TiO_2 nanocomposite help in the detection of ethylene in package responsible for fresh produce ripening (Pimtong-Ngam et al. 2007).

Electron-deficient diene- or triene-based systems

Some ethylene scavengers are based on electron-deficient dienes or trienes, for example benzenes, pyridines, diazines, triazines and tetrazines; these compounds have electron-withdrawing substituents, namely fluorinated alkyl groups, sulphones and esters (particularly dicarboxyoctyl, dicarboxydecyl and dicarboxymethyl ester groups), that react quickly and irreversibly with gaseous ethylene at 23 °C (room temperature) and eliminate ethylene from the package (Holland 1994). Such compounds can be incorporated into permeable polyethylene bags or printing inks to eliminate ethylene from fresh produce packages. The scavenger may also be used in the form of sachets and labels packaging applications. About 0.01–1.0 M of the dicarboxyoctyl ester derivative of tetrazine combined in polymeric films was confirmed to be able to affect a tenfold drop in ethylene gas in sealed jars in 24 h and a 100-fold reduction within 48 h (Brody et al. 2001). Scully and Horsham (2007) reported on the development of electron-deficient nitrogen-comprising trienes integrated with ethylene-permeable films. Nonetheless, in the presence of high moisture tetrazine is very unstable and hence it should be incorporated with hydrophobic plastic films (such as polyethylene, polypropylene, polystyrene) for high moist food such as fresh fruits and vegetable packaging applications.

Fig. 4 Ethylene scavenging process of titanium dioxide by photo-catalysis



Forms of ethylene scavengers for packaging applications

Ethylene scavenging compounds scavenge the in-package ethylene, leading to extend physiological qualities of fresh produce. The ethylene scavenging capacity in the closed package can be influenced by: (1) the nature and amount of used scavenging compounds, (2) stability of scavenging materials in the presence of high relative humidity inside a package, (3) the storage temperature (Gaikwad et al. 2017a, b). The ethylene scavenging capacity of selected material should be considered along with the intended fruits/vegetable application and expected shelf life when designing an ethylene scavenging packaging system for food having sensitivity towards ethylene. For fresh produce packaging applications, generally used forms of ethylene scavenging packaging systems are sachets and plastic films. The commercially well-established technique is to incorporate the use of sachets which do not disturb the structure of packaging materials.

Sachets

Sachet is a popular and commercially well-established form of ethylene scavenger. Ethylene scavenging packaging systems in the form of sachets are generally used to keep low levels or removal of ethylene in fresh produce packages (Yam 2010). In this form, ethylene scavengers are in the form of powder, granules, and beads, usually packaged in a porous material-based sachet. Rarely ethylene scavenging sachets, made of steel wire mesh, are available and follow from the range of porous slabs and blankets prepared for ethylene elimination in cold stores and shipping containers. $KmNO_4$ is the most common scavenging materials used in the sachets form due to safety concern. The commercial ethylene scavenging sachets used to scavenge and/or control ethylene inside fresh produce packages are SendoMate (Mitsubishi Gas Chemical Co. Ltd. Japan), Evert-Fresh (Evert-Fresh Corporation Ltd., USA), BRYSORBTM 508 (Bry-Air (Asia) Pvt. Ltd., India), Super Fresh Media (Ethylene Control, Inc., USA) and Biofresh (Grofit Plastics, Israel). Ethylene scavengers in the form of powders should not expose straight to high relative humidity environment. The dimensions of the sachet required for packaging subject to many variables including the fruits and vegetable type, the extent of time essential to protect the fresh produce, the weight of fresh produce, the size of the packaging to protect, the inception of sensibility to ethylene gas and many others. The main benefit of the sachets form is that they offer constant protection, from the packaging process line to the retail backroom, by eliminating ethylene all along the distribution supply chain. The application of such sachets is not suggested during extended storage periods with high ethylene-producing fresh produce because the ethylene scavenger may be speedily saturated, demanding regular sachet replacement.

Polymeric films

Various polymers and the diverse compositions are available for the manufacturer to implement a food packaging solution and develop most suitable to the specific needs of each product. Most polymeric films (polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), polyethylene terephthalate (PET)) of 10–60 µm thicknesses commonly employed in fresh fruits and vegetable packaging have a high water vapour transmission rate (WVTR) relative to the transpiration rates of fresh produce. Since sachets have limited consumer recognition, ethylene scavenging packaging in the form of polymeric films is increasing in popularity. In the last few years, numerous ethylene scavenging films based on PE incorporated with finely distributed powdered material, for example zeolite, clays and activated carbon, have existed. Presently, there are two approaches to incorporate these ethylene scavenging compounds in the packaging material; they can be introduced into the polymeric matrix via a melt extrusion process, or they can be applied as a coating. Most of the time, the selection of the incorporation process was based on the type of packaging to be used for packing fresh produce and the capacity of the manufacturer to incorporate the ethylene scavenger into its products. Recently, Siripatrawan and Kaewklin (2018) fabricated chitosan–titanium dioxide nanocomposite-based films using solvent casting method, Tas et al. (2017) developed halloysite nanotubes and polyethylene-based nanocomposites films using extrusion process, Singh and Giri (2014) developed $KMnO_4$ inserted onto SiO_2 crystals using low-density polyethylene (LDPE) film, which were developed. These functional ethylene scavenging films with incorporated clays may physically adsorb ethylene, but it shows low scavenging efficiency for eliminating it because of the low amount of clays that can be incorporated into polymer matrix without affecting the physical properties of the package such as barrier, mechanical properties (Singh et al. 2018c). Furthermore, they are opaque and course materials and hence incorporated clay's affect film gas barrier allowing CO_2 gas out more speedily and allowing O_2 to enter faster than regular plastic films. Zagory (1995) form a theory that the higher permeation of gases of these discontinuous materials might be the reason for improved quality and longer shelf life of highly perishable fruits and vegetables instead of ethylene scavenging efficiency of the clays. Biaxially oriented polypropylene (BOPP) films integrated with filler yield their microporous structure with controllability of gases (Nakamura et al. 1993), and hence, they could also be used to extend the shelf life of fresh produce. "BO film," promoted by Japan's Odja Shoji, is an LDPE film extruded with finely grind crysburite ceramic, claimed to confer ethylene scavenging capacity.

Applications of ethylene scavengers in fresh produce packaging

In the past, most of the research was based on the $KMnO_4$ effects on the physical and chemical quality attributes of fresh produce which has been studied. Several research studies based on the use of ethylene scavenger for fresh produce packaging applications are presented in Table 3. The number of researches about the effects of $KMnO_4$ on fresh produce was carried out on climacteric fruit, generally on apple and banana, mango which has a high ethylene-producing rate and highly ethylene sensitivity (Álvarez-Hernández et al. 2018). Postharvest quality of fresh produce is affected by many factors, such as physical injury, distribution, being storage managing the main factor to deliver a product with good quality, and extended shelf life, to the buyer. Storage management must take into account the rate of respiration, ethylene production and accumulation and sensitivity of the product to numerous critical parameters including storage temperature and initial gas concentrations, while high relative humidity rates should be maintained to extend fresh produce shelf life (Singh et al. 2018d).

Banana

Ripening of bananas is well known to be extremely dependent on the ethylene gas generated by bananas where the ethylene led green bananas to turn yellow and dark brown as they ripen. Hence, it is incredibly challenging to keep banana fruits in a good and fresh state for an extended period. Over the years, numerous researchers have worked on this issue, and the use of ethylene scavengers in banana packaging has been proved to be useful (Sen et al. 2012). Bananas are typically ripened by exposure to 50–100 ppm ethylene gas in a package. Galdi and Incarnato (2011) confirmed the prevention of the browning reaction in bananas using ethylene scavenger. Abe and Watada (1991) reported that charcoal in combination with palladium chloride as an ethylene absorbent, present in paper-based sachets and not in the packaging system, was active in inhibiting ethylene accumulation, plummeting the softening in fresh-cut bananas, and it was effective in absorbing most of the ethylene gas during 3 d of storage for banana at 20 °C conditions. Some authors pointed out that both titratable acidity (TA) and soluble solids content (SSC) increase during the storage period of banana fruits (Gaikwad et al. 2017a, b; Pongener and Mahajan 2017). However, it has been observed that changes in TA and SSC are delayed when an ethylene scavenger based on $KMnO_4$ is combined into the banana packages (Tzeng et al. 2019). Tas et al. (2017) developed novel halloysite nanotubes/polyethylene (HNT/PE) nanocomposites as an ethylene scavenging film neat PE film results showed that the banana-packaged NEAT PE film turned yellow, and several brown spots were observed; on the other hand, bananas packaged with HNT/PE films showed banana stayed free of brown spots and maintained green colour. Recently, Tzeng et al. (2019) developed and applied palladium-modified zeolite-based scavenger for delaying shelf life of a banana. Results showed that the palladium-modified zeolite delayed the ripening of banana and recovered its firmness and the peel colour of fruit significantly.

Ripening in bananas can also be hindered by using an ethylene scrubber. There are numerous complexes that can be used as inhibitors of ethylene gas, such as aminoethoxyvinylglycine, an inhibitor of ethylene synthesis, 1-methylcyclopropene, an inhibitor of ethylene action and $KMnO_4$, an oxidizing material. Particularly for the banana, 1-methylcyclopropene and $KMnO_4$ are the generally used ethylene scrubbers.

Apple

Being a climacteric fruit, apple results are highly sensitive to ethylene. It has been stated that low O_2 environment and high CO_2 levels in package synergically act to decrease ethylene accumulation and respiration rates in apple and however could not stop senescence and tissue breakdown (Soliva-Fortuny and Martín-Belloso 2003). Shorter et al. (1992) reported lower ethylene and CO_2 levels in packages of apple (*Grammy Smith*) stored in polyethylene bags at 0.5 °C for 2 weeks with $KMnO_4$ alumina pellet scrubbers. At the end of storage study, minor physical disorders including bitter pit and superficial scald were noticed in apples stored with the above ethylene scrubber. Decrease in firmness loss and delayed shell yellowing were observed when $KMnO_4$-based ethylene scavenger was utilized in the packaging of different varieties of apples such as Gala, Royal Gala, Golden Delicious and Brookfield. Recently, Li et al. (2011) tested active polyvinyl chloride (PVC) films coated with nanozinc oxide on freshly cut Fuji apples at 4 °C for 12 d. Nanocoated PVC film decreased decay rate, enzyme activity in fruits retarded ethylene production in package, and maintained degree Brix as well as titratable acidity when compared to uncoated PVC film. Highest ethylene content was 40 μL/kg d for nanopackaging and 70 μL/kg d for the control on day 9. All inclusive, it can be concluded that the application of ethylene scavengers in the package is a useful tool to reduce flavour alterations or differences in sugars

Table 3 Reports on the use of ethylene scavengers for fresh produce packaging applications

Ethylene scavengers	Application form	Fresh produce	Benefits	Reference
TiO_2	Chitosan film	Tomato	Delayed the ripening process and changes in the quality of the tomatoes stored at 25 °C and 50% RH	Kaewklin et al. (2018)
Potassium permanganate	NS	Guava	Shelf life of guava stored at 4 °C; 85% RH was extended to 32 days, retained a high amount of phenol and ascorbic acid, not affected by chilling injury or mould	Murmu and Mishra (2018)
Halloysite nanotube	LDPE Film	Strawberry, banana, tomato	The improved shelf life of bananas and tomatoes packaged with films stored at 4 °C	Tas et al. (2017)
Silica gel	NS	Pointed gourd	Reduced spoilage and disease index. Delayed up to 8 days chlorophyll content loss stored at 29.4–33.2 °C (68–73% RH)	Bhattacharjee and Dhua (2017)
Vermiculite	Sachet	Sapodilla	Delayed pulp firmness loss and vitamin C degradation. 25 °C (54% RH) for 5 days	de Souza et al. (2017)
Zeolite-based minerals	LDPE film	Kiwifruit	Extension of shelf life up to 20 d at 4 °C by establishing equilibrium atmosphere, higher sensory quality	Ahn et al. (2016)
Zeolite (clenoptelolite)	Filter	Peach	Reduced firmness and weight loss. Delayed pH increase. Maintained good appearance. A slight effect on SSC and TA was observed stored at 0 °C 36 days	Emadpour et al. (2015)
Zeolite-based various alumino-silicate minerals	LDPE films	Broccoli florets	Improvement of overall quality and increase in shelf life up to 20 d at 4 °C	Esturk et al. (2014)
Silica crystal	Sachet	Guava	Reduced changes in fruit firmness, SSC, TA and colour. Decay was reduced stored at 8 °C	Singh and Giri (2014)
Vermiculite	Sachet	Baby banana	Delayed peel yellowing. Slowed SSC increase and TA decrease. Reduced firmness loss and weight loss. minimized SSC/TA ratio increase storage condition: 18 °C 16 days (70–80% RH)	García et al. (2012)
Zeolite fine particles of mordenite framework inverted-type zeolite	LDPE film	Mango	Extension of shelf life up to 40 d at 12 °C, reduction in weight loss, maintaining firmness, no sign of decay	Boonruang et al. (2012)
Nano-Ag, nano-TiO_2 and montmorillonite	PE film	Kiwifruit	Inhibition of ethylene production (57.4% lower headspace ethylene concentration in nanopackaging), prevention of physiological changes, delay in ripening	Hu et al. (2011)

Table 3 (continued)

Ethylene scavengers	Application form	Fresh produce	Benefits	Reference
Nano-ZnO	PVC film coated with nano-ZnO	Fresh-cut apple	The reduction rate of in fruit decay, a slowdown in ethylene production, maintenance of °Brix and titratable acidity and inhibition of enzyme activity	Li et al. (2011)
Nano-Ag, nano-TiO_2 and kaolin	PE film	Strawberry	Quality improvement: sensory, physicochemical and physiological properties (decay rate, anthocyanin, and malondialdehyde contents were decreased for nanopackaging and normal packing, respectively)	Yang et al. (2010)
Nano-Ag, nano-TiO_2 and kaolin	PE film	Chinese bayberry	Controlling green mould decay, reduced respiration rate and ethylene production (49.6% and 25.9%, respectively, for combined treatment of hot air and nanopackaging which was lower than the control) and providing firmer fruit for 8 d at 1 °C	Wang et al. (2010)
Nano-Ag, nano-TiO_2 and kaolin	PE film	Chinese jujube	Positive effects on physicochemical and sensory quality, prevention of fruit softening, weight loss, browning and climatic evolution, and ethylene control (maximum ethylene content of 17.6 µL/kg h for the control on 3rd day and 9.2 µL/kg h for nanopackaging on the 6th day of storage)	Li et al. (2011)
Zeolite	Filter	Lettuce, iceberg	Reduced texture firmness loss and minimized colour changes. Delayed weight loss, pH reduction and tissue browning (21 days)	Kalaj et al. (2008)
Zeolite-based impregnated with $KMnO_4$	HDPE films	Kiwifruit	Firmer texture, higher vitamin C content, no shelf life provided	Küçük (2006)
A natural hygroscopic mineral (*not specified*)	Commercial LDPE bags (by Peakfresh)	Broccoli	Less weight loss, maintenance of chlorophyll content and improvement of colour and texture, the shelf life of 12 d at 4 °C and 9 d at 10 °C	Jacobsson et al. (2004)

PE: polyethylene; LDPE: low-density PE; HDPE: high-density PE; NS: not specified; Ag: silver, $KMnO_4$: potassium permanganate; TiO_2: titanium dioxide; PVC: polyvinyl chloride and free organic acid contents in apples during storage at low temperatures.

Tomato

Ethylene production leads to an increase in the biosynthesis of carotenoids in tomatoes. Recently, Kaewklin et al. (2018) developed chitosan-based ethylene scavenging films (Fig. 5) incorporated with nano-TiO_2 to preserve the quality and extend the storage life by 14 days of Korean cherry tomatoes. These films showed ethylene photo-degradation, which might contribute to delay the ripening and prolong the storage period of the most widely consumed fresh produce. In another study, the use of HNTs with high ethylene adsorption capability delayed the processes of softening and ageing of tomato (TAS et al. 2017). The efficacy of numerous ethylene scavengers that is palladium-supported nanozeolite, $KMnO_4$-supported nanozeolite, 1-methyl cyclopropane, salicylic acid on the maintenance of the postharvest quality of tomato fruits was recently evaluated. Results showed that the palladium-supported nanozeolite is the tool which contributes to shelf life extension as well as the preservation of quality parameters of tomato fruits during storage. The palladium-supported nanozeolite had 5% additional positive effects, particularly on phenolic and lycopene contents, polygalacturonase activity, fruit firmness and weight loss (Mansourbahmani et al. 2018). Mujtaba et al. (2014) found that packaging of tomato (*Rio Grandi*) into polyethylene films combination with a $KMnO_4$-based ethylene scavenger can lower ascorbic acid increment, make acidity to increase and delay lycopene biosynthesis, deprived of effects on tomato pH.

A research study by Bailen et al. (2006) states that combination of MAP and activated carbon enhanced the sensory properties, lower the decay, and enriched the quality attributes of freshly harvested tomatoes compared to MA packages without activated carbon. The witnessed effect was attributed to the properties of activated carbon to act as an ethylene scavenger. The scavenging effects were more prominent with the application of activated carbon and palladium.

Mango

Boonruang et al. (2012) packaged mango in four different packaging films and stored at 12 °C. The tested films were non-perforated, high gas permeability, a non-perforated high gas-permeable film with ethylene-absorbing property, microperforated high gas-permeability film and neat low-density polyethylene film. The non-perforated film was having ethylene scavenger prolonged the shelf life of mango up to 40 d at 12 °C, as compared to 35 d with the non-perforated, high gas-permeable film, 30 d with the microperforated film, and 5 d with the pure low-density polyethylene. The film with ethylene scavenger decreased weight loss, preserved firmness, and no sign of decay during the storage period. Here, the ethylene scavenging properties of the packaging material

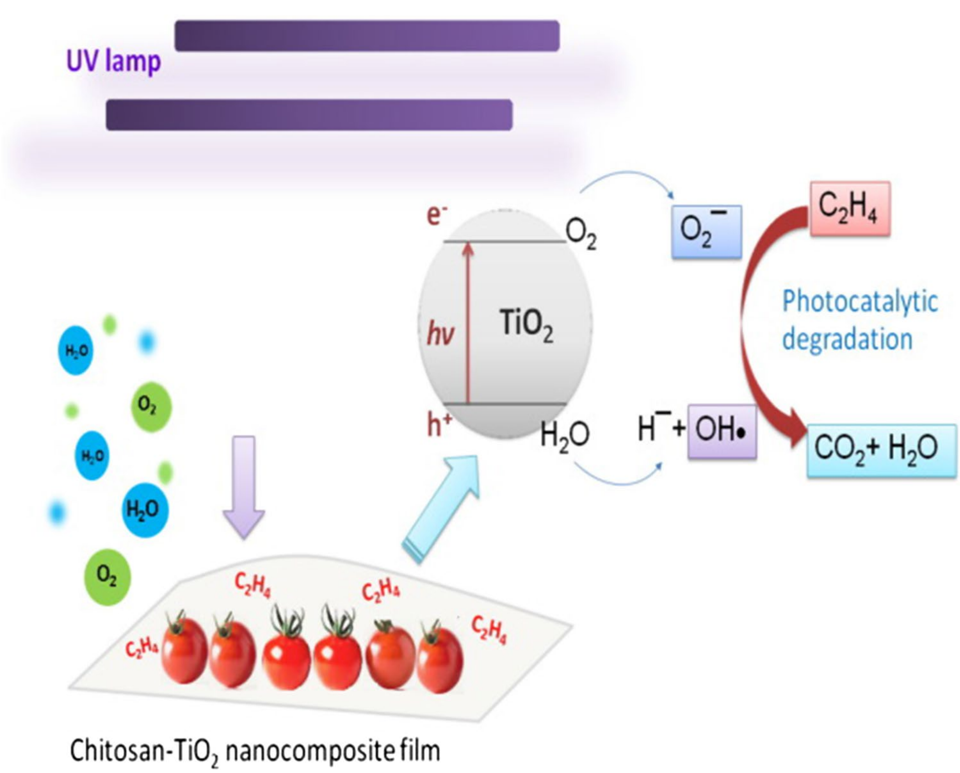


Fig. 5 Activation of titanium dioxide in the film to oxidize ethylene when exposed to UV light

delayed the ripening process in mangoes. Recently, Jaimun and Sangsuwan (2019) developed ethylene scavenging paper for mango packaging using vanillin–chitosan coating with varying amount of zeolite or activated carbon at 0, 0.1, 0.2 and 0.4%, (w/v) of ethylene scavenger on bleached paper and wrap on commercial mango fruit (*Nam Dok Mai*) to study the quality change in 30 days. Results exhibited the changes in weight loss, firmness, titratable acidity, and total soluble solids, and surface colour of selected mango fruits covered in zeolite paper (0.2%) was quite low, compared with those wrapped with uncoated papers.

Safety aspects and economic concerns

Even though scientific inventions in ethylene scavenging packaging can improve the safety and maintain the quality of fresh produce, safety concerns and confines should be considered. Such concerns and confines consist of the migration of active materials from packaging material to fresh produce, accidental leakage of active materials from a sachet to fruits, and accidental human ingestion of active materials. Ethylene scavenging sachets used in fresh produce packages should be marked "do not eat," or they should be exchanged by directly integrating active materials into or onto the package. The food safety concerns ethylene scavenging packaging should be based on the following three main parameters,

1. Labelling on the package of fresh produce, with the purpose to prevent misuse and misinterpretation by the consumers, for example to avoid sachets from being consumed.
2. Migration of scavengers should be sensibly considered in addition to all breakdown products, a function of their toxicity—for example $KMnO_4$ toxicity. Measuring migration indicates to develop dedicated migration tests along with mass transfer modelling tools since those existing, or suggested for conventional polymers, are not adapted to ethylene scavenging systems.
3. Effectiveness of the packaging, in a few cases, and the capability of the packaging to achieve the ethylene scavenging function can raise safety problems as for any food preservation technology.

Consumer acceptance of active packaging can be partial by health and environmental safety concerns (risk perception) and suspicion of new technologies, which is due to a lack of proper information about new technologies involved.

As we know, fresh produce relatively low cost, compared to other food products and hence high packaging cost, increases the final cost of fresh produce. The commercial application of new ethylene scavenging packaging might cause an increase in single product unit costs and prices, particularly during the primary phases of product introduction, which may indirectly affect customer's behaviour and acceptance of the product (Dainelli et al. 2008). From the producer's viewpoint, the income margins of food are somewhat low compared to those of other consumer products (Singh et al. 2018). Consequently, the use of innovative packaging in the fresh produce industry should be based on appropriate cost–benefit considers justifying their application (Gaikwad et al. 2018a). Additionally, research and development in the field of ethylene scavenging packaging materials represent a possible path towards lower final product cost without affecting enhancements in food shelf life. Further, the major obstacle for ethylene scavenging packaging is undoubtedly to design functional materials capable of maintaining their original mechanical and barrier properties, and concurrently confirming the scavenging activity of the active agents during the entire process of distribution, storage and handling as packaging materials. Further fundamental difficulties comprise technology transfer, manufacturing process scale-up, food regulatory requirements for safety, environmental concerns, and most importantly, consumer acceptance (Werner et al. 2017).

Conclusion

Ethylene scavenger containing active packaging is a promising future path for the growth of highly ethylene-sensitive fresh produce packaging. It is confirmed that the use of ethylene scavenger in the package could extend the shelf life and maintain the physical quality of fresh produce. Hence, the parallel application of various types of ethylene scavenging system incorporated in film form not only satisfies consumer demands for replacement of synthetic preservatives and plastics but also brings stronger protective effects from excess ethylene in the fresh produce. At the time of choosing the appropriate ethylene scavenging system or form of packaging for ethylene gas regulation, it is crucial to know the physiological characteristics of the fresh produce. Nevertheless, the growth and application of ethylene scavenging packaging will depend on the acceptance and cost-effectiveness for the fresh produce growers, processing industry and consumers. Hence, extra effort should be focused on overcoming the technological limitations and high costs related to these technologies, which have been the key factors inhibiting more comprehensive implementation and the development of additional commercial applications for ethylene scavenging materials in the food processing and packaging industries.

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