



Review

Oxygen scavengers for food packaging applications: A review

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ABSTRACT

Background: Many food products available are sensitive to oxygen and which upon prolonged exposure may lead to deterioration in the food quality like change in taste, odour and colour of the food or facilitate the growth of microorganisms in them. Addition of oxygen scavengers is one of the means to reduce the oxygen exposure on food products. Oxygen scavengers are a type of active packaging technique which absorb the dissolved oxygen or oxygen in the headspace leading to extended shelf life and retainment of the original food quality.

Scope and approach: Extensive work has been done in this particular field. In this review, oxygen scavenging systems like iron, palladium, ascorbic acid, tocopherol, unsaturated hydrocarbons, microorganisms have been thoroughly discussed along with their applicability with respect to the moisture content of the targeted food products. The mechanism of action of the respective systems are also explained adequately.

Key findings and conclusion: Many naturally occurring oxygen scavengers based on phenolic compounds and naturally occurring minerals like hydrotalcite have been mentioned in this review which have not yet been investigated thoroughly. Not much research has been done on zero valent metals like copper etc as oxygen scavenger.

1. Introduction

Packaging of food is generally referred to a technique of providing a barrier to protect food from unwanted environmental disturbances such as oxygen, moisture, light, dust, and both chemical and microbiological contamination, also known as passive packaging (Yildirim et al., 2018). Over the years, the packaging technology has evolved leading to the development of Modified Atmosphere Packaging (MAP) and Active Packaging (AP). Modified atmosphere packaging is an approach of extending the shelf life of food and maintaining their initial freshness by changing the atmosphere around the food in a specific composition, hence slowing down the deterioration process of fresh cut vegetables and meat (Sandhya, 2010) (Manolopoulou & Varzakas, 2013) (Fraqueza & Barreto, 2011). Although MAP was successful to maintain the freshness to some extent, active packaging was introduced which is a technique of prolonging shelf life of food products and maintaining their quality by incorporating some absorbers or emitters leading to a better result (Yildirim et al., 2018). The types of active packaging include oxygen scavengers, ethylene absorbers, carbon di-oxide emitters, antimicrobial packaging, moisture scavengers, antioxidant releasers etc. Presence of moisture can affect the quality of food by changing its texture, appearance or making it susceptible to microbial damage (Labuza & Hyman, 1998). To prevent this, some dessicants like clay,

silica, zeolites are generally used. Other commonly used materials for this purpose include bentonite and poly-acrylic acid sodium salts (Mahajan, Rodrigues, Motel, & Leonhard, 2008) (Azevedo, Cunha, Mahajan, & Fonseca, 2011). Ethylene accelerates ripening and chlorophyll degradation in fresh and leafy products shortening their shelf life (Saltveit, 1999), hence ethylene scavengers like potassium permanganate, zeolites and nanoparticles are used to avoid the food degradation (Hu, Fang, Yang, Ma, & Zhao, 2011) (Llorens, Lloret, Picouet, Trbojevich, & Fernandez, 2012). Systems based on ferrous carbonate or a mixture of ascorbic acid and citric acid act as carbon-dioxide emitters which suppress the growth of microbes leading to a longer shelf life of packaged food (Suppakul, Miltz, Sonneveld, & Bigger, 2003). Other antimicrobial packagings include incorporation of nanoparticles (mainly silver, gold or metal oxide nanoparticles); antimicrobial polymers like chitosan; enzymes (Youssef, El-Sayed, El-Sayed, Salama, & Dufresne, 2016) (Panea, Ripoll, González, Fernández-Cuello, & Albertí, 2014). Nanoparticles as antimicrobial agent have gained popularity accounted to their inhibiting or retarding effect on the growth of microorganisms. The antimicrobial activity of silver nanoparticles can be explained by their attachment to the cell surface followed by penetration inside the cell and DNA damage (Honarvar, Hadian & Mashayek, 2016). Finally synthetic antioxidants like butylated hydroxytoluene (BHT) and butylated hydroxyanisole (BHA) are used to prevent lipid

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oxidation in foods (Torres-Arreola, Soto-Valdez, Peralta, Cárdenas-López, & Ezquerro-Brauer, 2007).

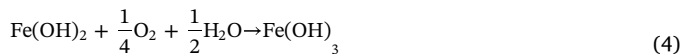
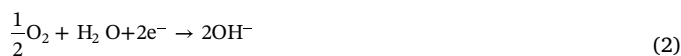
After successful application of packaging techniques, it is important to monitor the quality of the packaged food. Intelligent packaging is capable of carrying out functions like detecting, recording, tracing etc. to facilitate decision making to extend shelf life and improve quality of food. The latest advances in smart package devices include indicators, data carriers and sensors. The indicators provide information about the presence or absence of a substance. They commonly include temperature sensors indicating a fallacy by changing colour; freshness indicator based on volatile content or hydrogen sulfide content; and gas indicators which notify the change in inside atmosphere. Secondly, the data carriers are incorporated to enhance traceability and to prevent theft. A specific pattern of bars and spaces, also known as barcode; or a tag that can emit radio waves also known as radio frequency identification are some commonly used data carriers (Ghaani, Cozzolino, Castelli, & Farris, 2016) (Yam, Takhistov, & Miltz, 2005). Using nano-sensors over conventional, costly and time consuming detection methods like HPLC have advantages including ease of operation, speed, less power requirements for detection of chemical compounds, toxins, microbes or change in environmental factors like temperature or oxygen (Honarvar, Hadian & Mashayek, 2016).

2. Oxygen scavengers

Presence of oxygen in food packages lead to rapid spoilage of food due to rapid oxidation of fats or vitamins present in food, or by promoting the growth of microorganisms like aerobic bacteria, yeasts and moulds. Hence the above mentioned factors result in a change in colour, smell or taste of food (Jacobsen, 1999) (Jacobsson, Nielsen, & Sjöholm, 2004). Vacuum packaging is an approach to create an oxygen free environment in food packages (Narasimha Rao & Sachindra, 2002). Another approach in oxygen removal from headspace of food packaging is MAP, a technique of modifying the atmosphere of packaging. MAP is a more versatile technique compared to vacuum packaging which relies solely on removing oxygen from the headspace. MAP on the other hand can be tailored according to the food product (Narasimha Rao & Sachindra, 2002). It has been found that MAP proves itself to be beneficial in some food packaging like smoked trout (“Đorđević et al., 2017), beef (Hur, Jin, Park, Jung, & Lyu, 2013) and rabbit meat (Rodríguez-Calleja, Santos, Otero & García-López, 2010) whereas in other cases like packaging of dry cured ham (García-Esteban, Ansorena, & Astiasarán, 2004), both MAP and vacuum packaging produced comparable results. However, it was found that vacuum packaging or MAP can reduce the residual oxygen level in the headspace up to only 0.5–2 vol% which may prove itself to be destructive (Gibis & Rieblinger, 2011). On the contrary, oxygen scavengers may reduce oxygen level to less than 0.1 vol% leading to an extended shelf life (Mills, Doyle, Peiro, & Durrant, 2006). The current review focuses on different types of oxygen scavengers which are commonly used to enhance the food quality and shelf life. Additionally, this review also includes new types of oxygen scavengers being used and under development stages other than the conventional ones mentioned in the literature previously. Also commercially used oxygen scavengers are mentioned.

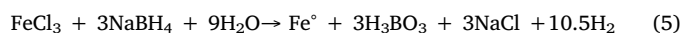
2.1. Iron based scavenging systems

The most commonly used oxygen scavenger for commercial purposes are iron powder sachets. These scavengers are based on the principle of oxidation in presence of moisture or Lewis acids like FeCl₃ or AlCl₃ (Cruz, Soares, & Andrade, 2006) (Rollick, 2010). The mechanism of oxidation can be described by the following reactions (Cruz, Camilloto, & dos Santos Pires, 2012):



The iron sachets were used as oxygen absorbents along with vacuum technology for preservation of lasagna pasta. It was observed that the growth of microorganisms like yeast, moulds or coliforms was very slow and did not reach the maximum allowable limit till 30 days, from which it can be justified that iron can be used as an effective scavenger for oxygen (Cruz et al., 2006). The iron powder can also be impregnated in polymeric films resulting in an increased surface area, leading to better scavenging capacity. The change in scavenging capacity with change in polymer used can be accounted to the varying oxygen permeability of the polymers (Beckwith et al., 2009). Food samples like sausages were packaged with iron powder containing polymer films which showed a scavenging capacity of 33 cm³O₂/m²film in 4 days. It was observed that with increase in temperature, the absorption of oxygen increased (Gibis & Rieblinger, 2011).

Nanoiron on the other hand showed oxygen scavenging activity both in presence of moisture and anhydrous environment as well (Foltynowicz et al., 2014). The nanoiron was produced by reduction of an iron salt in presence of sodium borohydride.



When compared with iron particles in micrometer size, nanoiron showed better scavenging capacity (Foltynowicz, Bardenshtein, Sänglerlaub, Antvorskov, & Kozak, 2017) (Mu et al., 2013). It was observed that using nanocomposites made of polymeric films, montmorillonite (OMMT) and iron nanoparticles affected the physical and mechanical properties of the packaging. Addition of 2 wt% OMMT to polypropylene films reduced the oxygen permeability and water vapour permeability by 22% and 33% respectively, while addition of 0.2 wt% of iron nanoparticles resulted in reducing oxygen permeability by 55% and increased the scavenging capacity by 77% (Khalaj, Ahmadi, Lesankhosh, & Khalaj, 2016). Table 1 lists some of the prominent literature involving iron both in nanometer and micrometer range used as oxygen scavengers.

2.2. Platinum group metals based scavenging systems

Platinum and palladium are generally used in food packaging accounted to their low toxicity and high efficiency in catalyzing the conversion of hydrogen and oxygen into water (Yu et al., 2004). Thus in presence of a modified atmosphere containing hydrogen, they can act as an oxygen scavenger for food packaging (Nyberg & Tengstål, 1984). It was observed that the metal helped in the reaction of oxygen in presence of small amount of hydrogen resulting in a reduced oxygen level by two orders of magnitude (Yu et al., 2004). Metals or their compounds along with reducing agents were anchored to polymeric films for food packaging. The scavenging capacity changed with the change in oxygen permeability of the polymers. The atmosphere of the packaging were modified by flushing with hydrogen gas to enhance the reaction (Hutter, Rüegg, & Yildirim, 2016) (Elsome, Pratt, & Slade, 2003). In some other cases a hydrogen generating agent like sodium borohydride was added (Akkapeddi, 2014) (Carmichael et al., 2014). Addition of chlorine with palladium catalyst enhanced the distribution of the catalyst leading to higher efficiency. Also, sodium and iron acted as promoters in the catalyzing reaction (Quesada, 1969) (Quesada & Neuzil, 1969). The technology was applied and found apt for food packaging of materials like ham, vitamin C, wine, tea and fruit juices (Hutter et al., 2016) (Carmichael et al., 2014). Palladium used as oxygen scavengers for various packaging has been suggested in Table 2.

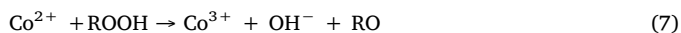
Table 1

Oxygen scavenging packaging with iron in active layer.

Oxygen Scavenging Active Layer	Key Findings	Reference
Nano iron + polymer	<ul style="list-style-type: none"> Scavenging capacity of nanoiron is 300 cm³ of oxygen in 5–6 days. Moisture or CO₂ does not effect the scavenging capacity significantly. Nanoiron + silicon matrix scavenged 100% oxygen in 3 days Nanoiron + nylon 6,6 films scavenged 100% oxygen in 6 days. Nanoiron + PVA films scavenged 100% oxygen in 4 days. Nanoiron + PE films removed oxygen only partially. 	((Foltynowicz et al., 2014)
Nanoiron and Conventional Iron powder	<ul style="list-style-type: none"> Food sample used- roasted peanuts Nanoiron <ul style="list-style-type: none"> oxygen scavenging rate - 0.45 ± 0.044 h⁻¹ oxygen absorbed - 130 ml of O₂ in 15 h. conventional iron powder <ul style="list-style-type: none"> oxygen scavenging rate - 0.05 ± 0.006 h⁻¹ oxygen absorbed - 90 ml of O₂ in 50 days. 	Mu et al. (2013)
Iron + Polypropylene	<ul style="list-style-type: none"> The oxygen scavenging capacity of the stretched films was found to be 3.49 cc of O₂/gm of film. 	Chau (2015)
Iron + (FeCl ₃ /AlCl ₃) + Polyethylene terephthalate	<ul style="list-style-type: none"> The maximum amount of scavenged oxygen in 4 days Fe⁰/FeCl₃ - 0.102 cc O₂ per gram of polymer Fe⁰/AlCl₃ - 0.18 cc O₂ per gram of polymer 	Rollick (2010)

2.3. Unsaturated hydrocarbon based scavenging systems

A high capacity oxygen scavenging technique includes oxidation of unsaturated hydrocarbons for food packaging purpose. The main advantage of this kind of scavenging system lies with the fact that they can be used to package dry foods. One of the most commonly used hydrocarbon for scavenging purpose is 1,4- polybutadiene along with cobalt neodecanoate as the catalyst. The reaction mechanism as suggested by Li et al. (2012) is:



where the RH refers to the allylic carbon hydrogen bonds of the polymer which are most susceptible to undergo oxidative degradation. It was observed that the scavenging rate increased with the increase in catalyst loading. A sample containing 1000 ppm of cobalt neodecanoate scavenged 9 mg of O₂/100 mg of polymer while sample with 400 ppm of cobalt neodecanoate scavenged 2 mg of O₂/100 mg of polymer (Li et al., 2012). It was also observed that the scavenging capacity increases with increase in temperature (Cahill & Chen, 2000) (Speer & Roberts, 1994). A major disadvantage of this type of system is production of odour causing by-products. Miranda and Speer (2005) suggested addition of a barrier layer which could impede the migration of the by-

products into the food.

Cut apples were packed with an oxygen scavenging layer consisting of polyamides and polyethylene terephthalate as the barrier layer. It was found that the oxygen transmission rate decreased with addition of the oxygen scavenging layer. There was no change in colour of the cut apples, suggesting the ability of the system as an effective oxygen scavenger (Di Maio, Scarfato, Galdi, & Incarnato, 2015). Various examples of unsaturated hydrocarbons as oxygen scavengers along with the effect of temperature and catalyst on scavenging activity has been mentioned in Table 3.

2.4. α-Tocopherol based scavenging systems

α-tocopherol is a promising option for food packaging application as it a natural free radical scavenger (Hamilton, Kalu, Prisk, Padley, & Pierce, 1997). The α-tocopherol is generally combined with a catalyst which enhances the scavenging activity due to the non-enzymatic reaction between oxygen and the transition metal followed by free radical scavenging by tocopherol. Some commonly used catalysts include iron (II), copper, manganese and cobalt. The scavenging mechanism as proposed by Byun, Darby, Cooksey, Dawson, and Whiteside (2011) is:

**Table 2**

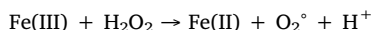
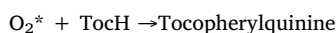
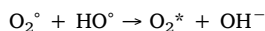
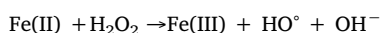
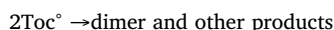
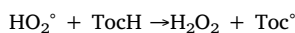
Oxygen scavenging packaging with palladium in active layer.

Oxygen scavenging active layer	Key Findings	References
Palladium + PET/SiOx films	<ul style="list-style-type: none"> Food Sample used- Ham oxygen concentration reduced from 2 vol% to 0.47 vol% in 2 min Palladium preserved the ham and prevented its discolouration for 21 days. 	Hutter et al. (2016)
Palladium + Alumina support	<ul style="list-style-type: none"> Activity of the reference catalyst with 0.5% palladium + 0% iron- 100 Activity of catalyst with 0.5% palladium + 0.2% iron – 125 Activity of catalyst with 0.5% palladium + 0.21% iron + 0.44% sodium – 188. 	Quesada and Neuzil (1969)
Palladium + Polymer	<ul style="list-style-type: none"> The oxygen scavenging capacity of 10 mg of 10% Pd varied with different polymers. The oxygen reduced from 1% to <ul style="list-style-type: none"> 0.3% in 60 min - ethyl cellulose 0.17% in 75 min - polyurethane 0.31% in 123 min - polyvinyl buytyral 0.15% in 200 min - nitrocellulose 0.28% in 91 min - silicone rubber 	Elsome et al. (2003)
Palladium + Polymer	<ul style="list-style-type: none"> Oxygen scavenging increased with increase in palladium content. The oxygen content reduced from 14000 ppm to <ul style="list-style-type: none"> 0 ppm in 110 min with 4 wt% palladium 2500 ppm in 175 min with 2 wt% palladium. 	Ekman, Murrer, Peltonen&Sundell (2006)

Table 3

Oxygen scavenging packaging with unsaturated hydrocarbons in active layer.

Oxygen Scavenging Active Layer	Key Findings	Reference
1,2-polybutadiene + cobalt benzophenone + poly (ethylene vinylacetate)	The oxygen scavenging rate with change in temperature were <ul style="list-style-type: none"> • 450 cc O₂/m²/day at 25 °C • 24 cc O₂/m²/day at 4 °C 	Speer and Roberts (1994)
Polyethylene + Oxygen scavenging polymer films	<ul style="list-style-type: none"> • Food Sample used: Orange juice • Oxygen scavenger used: Styrene/Butadiene/Styrene containing 1000 ppm cobalt ion and 1000 ppm of benzoylbiphenyl initiator. • The dissolved oxygen reduced from <ul style="list-style-type: none"> - 2.5 to 0.3 mg/l in 6 weeks in presence of oxygen scavenging film - 3.8 to 3.4 mg/l in 6 weeks in absence of oxygen scavenging film 	Jerde et al. (2003)
Nylon-6+ Polybutadiene + cobalt	<ul style="list-style-type: none"> • The oxygen transmission rate (OTR) changed with the amount of polybutadiene in the sample. The OTR were: <ul style="list-style-type: none"> - 2 wt% PBD - 0.4 cc/100 in²/atm day - 3 wt% PBD - 0.097 cc/100 in²/atm day. 	Akkapeddi, Kraft, and Socci (2002)
Block co-polymer	<ul style="list-style-type: none"> • Oxygen scavenging capacity <ul style="list-style-type: none"> - 1,6 Hexanediol/Tetrahydrophthalic Anhydride Polyester- Poly (ethylene-co-1,2-butylene)diol – 32.3 cc/m².day - 60% 1,6 Hexanediol/Tetrahydrophthalic Anhydride Polyester- 40% polycaprolactone – 382 cc/m².day - 67% 1,6 Hexanediol/Tetrahydrophthalic Anhydride Polyester- 33% polylactic acid – 22 cc/m².day 	(Ebner & Berrier, 2010)
Terpolymers + Co-polyester powder + Cobalt stearate	<ul style="list-style-type: none"> • Terpolymer 1–39.6% Cyclic Butylene Terephthalate + 49.5% hydroxyl terminated functionalized polybutadiene + 9.9% epoxy functional styrene acrylic polymer. • Terpolymer 2–44.55% Cyclic Butylene Terephthalate + 49.5% hydroxyl terminated functionalized polybutadiene + 4.95% epoxy functional styrene acrylic polymer. • Oxygen transmission rates were: <ul style="list-style-type: none"> - 98.8% co-polyester powder + 0.6% terpolymer 1 + 0.6% cobalt stearate – 0.0225 cm³/pkg.day after 4 months - 98.8% co-polyester powder + 0.6% terpolymer 2 + 0.6% cobalt stearate – 0.0199 cm³/pkg.day after 4 months. 	(Hu & Avakian, 2012)
Polyethylene Terephthalate (PET) with residues of terephthalic acid, ethylene glycol and isophthalic acid + Transition metals	<ul style="list-style-type: none"> • OTR after 10 days <ul style="list-style-type: none"> - PET + 8 ppm Li + 10 ppm Al + 30 ppm P – 1.17 µl/day - PET + 8 ppm Li + 10 ppm Al + 75 ppm P – 1.93 µl/day - PET + 45 ppm P + 215 ppm Sb + 60 ppm Zn – 1.60 µl/day 	Stewart and Armentrout (2010)
Polybutadiene (PBD) functionalized with maleic anhydride (MA) or p-Aminobenzamide (p-ABA) + Cobalt/Manganese	<ul style="list-style-type: none"> • The oxygen ingress rate in the bottles decreased with functionalization of polybutadiene. The maximum oxygen ingress from 0 ppm as observed was: <ul style="list-style-type: none"> - PBD + Co - 2 ppm in 100 days - PBD + MA + Co- 2 ppm in 360 days - PBD + MA + p-ABA + Co - 1.1 ppm in 240 days • The oxygen ingress in the bottles was more when manganese was used as catalyst compared to cobalt <ul style="list-style-type: none"> - PBD + p-ABA + Mn - 2 ppm in 180 days - PBD + p-ABA + Co - 2 ppm in 260 days 	Knudsen and Murray (2014)



To avoid quick degradation, α -tocopherol was encapsulated in Poly-lactic acid (PLA) microparticles (Scarfato, Avallone, Galdi, Di Maio, & Incarnato, 2017) or loaded on PLA films (Di Maio, Scarfato, Avallone, Galdi, & Incarnato, 2014) for use in packaging purposes. It was observed that the encapsulation only resulted in slight change of scavenging activity but was advantageous for storage and handling. Similar approach was used by Noronha, De Carvalho, Lino, and Barreto (2014) to avoid oxidation of fatty foods. Methylcellulose coated α -tocopherol was used for the purpose which resulted in burst release of α -tocopherol in the first hour followed by sustained release in the next 10 days. Active films containing α -tocopherol was used to extend the life of salmon fish by Barbosa-Pereira et al. (2013). It was observed that the lipid oxidation in films reduced by 70% due to storage in the films. A comparison between α -tocopherol and other natural antioxidants like

trimethylhydroquinone was made by Byun and Whiteside (2012) which exhibited that α -tocopherol acted as a better scavenger as compared to others. Oxygen content reduced from 20.9% to $17.83 \pm 0.35\%$ and $18.37 \pm 2.14\%$ in 60 days in presence of α -tocopherol and trimethylhydroquinone respectively. Table 4 enlists the usage of α -tocopherol as oxygen scavenger and the effect of catalyst and moisture on the scavenging activity.

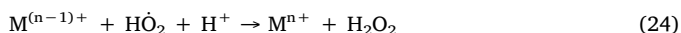
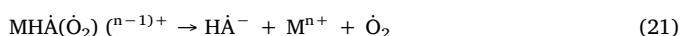
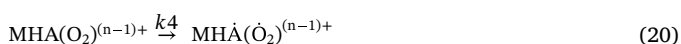
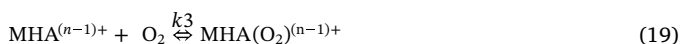
2.5. Ascorbic acid based scavenging systems

The scavenging action of ascorbic acid is based on the oxidation of ascorbic acid (AH₂) to dehydroascorbic acid (A). The scavenging action by ascorbic acid is slow and is enhanced in presence of catalysts like copper or iron. In case of uncatalyzed oxidation, the rate is dependent on the concentration of oxygen present while that in catalyzed reaction it is dependant on the formation of metal-ascorbate complex formed (MHA). The mechanism proposed is as follows where MHA (O₂) is a complex formed in intermediate and AH⁻ is the semiquinone form (Khan & Martell, 1967):



Table 4
Oxygen scavenging packaging with α -tocopherol in active layer.

Oxygen Scavenging Active Layer	Key Findings	References
α -tocopherol loaded PLA microparticles	<ul style="list-style-type: none"> Rate of oxygen scavenging was found to be <ul style="list-style-type: none"> 0.12 ml O_2/g.day - pure α-tocopherol 0.11 ml O_2/g.day - α-tocopherol loaded PLA microparticles 	(Scarfato, Avallone, Galdi, Di Maio, & Incarnato, 2017)
α -tocopherol + PLA films	<ul style="list-style-type: none"> Oxygen content decreased from around 19.5%–18.75% in 150 h for pure α-tocopherol Oxygen content decreased from around 19.5%–18% in 150 h for α-tocopherol loaded PLA films 	Di Maio et al. (2014)
α -tocopherol + PCL + iron (II)chloride films	<ul style="list-style-type: none"> Film contained 100 mg of iron (II) chloride and 50 μl water Scavenging rate-0.21 cm^3 of O_2 g^{-1} day$^{-1}$ The oxygen content in a batch with 50 mg iron (II)chloride decreased from 20.8% to 20.4%; whereas that in a batch with 0 mg iron (II)chloride decreased from 20.8% to 20.6% in 30 days. Increased moisture content decreased the scavenging capability. The oxygen content in a batch with 50 μl water decreased from 20.8% to 20.4%; whereas that in a batch with 0 μl water decreased from 20.8% to 19.6% in 30 days. 	(Byun, Whiteside, Cooksey, Darby, & Dawson, 2011)



The effect of transition metal on scavenging was evaluated and it was observed that presence of the metal ions Fe^{2+} and Cu^+ enhanced the scavenging activity by about 16.4% (Uluata, McClements, & Decker, 2015).

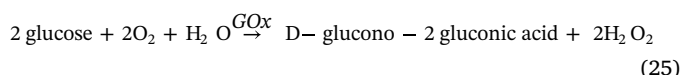
pH of the films play an important role in prevention of early oxidation as at different pH levels, different forms of ascorbic acid are predominant. At low pH, the fully protonated form (AH_2) is more stable and has much less susceptibility towards oxygen compared to ascorbate monoanion (AH^-) which is predominant at higher pH (Janjarasskul, Min, & Krochta, 2013). Min and Krochta (2007) used ascorbic acid incorporated whey protein isolate film to avoid lipid oxidation in roasted peanuts. Once applied to food at high pH, the ascorbate monoions are formed instigating the scavenging mechanism.

Another factor affecting the scavenging capacity of ascorbic acid in food packages is the water activity. Water activity is a measure of the unbound, free water in a food available to support biological and chemical reactions. It was observed that with its increase, the half life of the films decreased rapidly, or in other words the scavenging rate increased (Janjarasskul et al., 2013). A multilayer film approach by Mahieu, Terrie, and Leblanc (2017) suggested that addition of an extra poly-caprolactone layer along with a starch layer containing ascorbic acid, increased the mechanical strength of the films which proves to be beneficial for industrial application. The scavenging activity increased with increase in relative humidity. The films scavenged 13.5 ml of O_2 /g film in 15 days (Mahieu, Terrie, & Youssef, 2015). Sangatash, Niazmand, Jamab, and Modaressi (2016) studied the effectiveness of sodium ascorbate incorporated in polymeric sheets in oxygen scavenging to lessen the rancid oxidation in peanuts. The oxygen transmission rate (OTR) decreased on addition of 10% sodium ascorbate. The bacterial, yeast and mould count were found to be within limits. Effect of pH and water activity on the activity of ascorbic acid as oxygen scavengers have been listed in Table 5.

2.6. Enzyme based scavenging systems

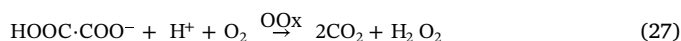
The most commonly used enzymes for oxygen scavenging in food packaging are glucose oxidase (GOx) along with catalase (Cat) (Strobel

& Gagnon, 1998) (Johansson, Jönsson, & Järnström, 2011). The scavenging takes place by the following mechanism where glucose must be present in food or in the scavenger formulation. The catalase added is introduced to break down the H_2O_2 formed during the reaction (Cruz et al., 2012).



The formation of gluconic acid reduces the pH and the effect of reduction in pH was not found to be detrimental (Johansson et al., 2011). Addition of clay in the polymeric or latex matrix led to increase in scavenging activity as clay plays an important role in prevention of pre-oxidation of glucose. Also the addition of clay increased the porosity of the films leading to higher substrate availability and hence increased scavenging activity (Nestorson, Neon, Kang, Järnström, & Leufvén, 2008) (Johansson et al., 2011). Presence of $CaCO_3$ along with the enzymes exhibited positive effects as $CaCO_3$ neutralizes the gluconic acid fomed. Also CO_2 is formed in the neutralization process which compensates for the decrease in pressure due to consumption of oxygen (Andersson, Andersson, Adlercreutz, Nielsen, & Hörnsten, 2002). Glucose oxidase and catalase has been used for protection of cheese and other refrigerated food products as per Sarett and Don (1956).

Oxalate oxidase (OO_x) along with catalase (Cat) has been used by Winstrand, Johansson, Järnström, and Jönsson (2013) as an effective packaging material because of its capability to scavenge oxygen as well as produce carbon dioxide which results in an increased shelf life in food items. The catalase degrades the hydrogen peroxide produced in the reaction catalyzed by oxalate oxidase. The mechanism followed is:



Another enzyme laccase has been used as oxygen scavenger where laccases are copper containing oxyreductases obtained from plants and fungus like *Trametes versicolor*, *Myceliophthora thermophila*, and *Rhus vernicifera* (Chatterjee, Johansson, Järnström, & Jönsson, 2011). This type of oxygen scavenging system was highly recommended for high moisture content food materials as the activity of the enzymes depend on high relative humidity. Various enzymes acting as oxygen scavengers have been shown in Table 6.

2.7. Micro-organisms based scavenging systems

Oxygen scavenging based on microorganisms entrapped in solid

Table 5
Oxygen scavenging packaging with ascorbic acid in the active layer.

Oxygen scavenging active layer	Key Findings	Reference
Ascorbic Acid + Whey protein isolate film	<ul style="list-style-type: none"> The O₂ scavenging capacity of the films with varying amount of ascorbic acid were <ul style="list-style-type: none"> 0.05 M - 8.9 ± 0.6 cc O₂/g dry film 0.1 M - 17.8 ± 1.2 cc O₂/g dry film 0.2 M - 35.6 ± 2.3 cc O₂/g dry film Oxygen permeability of the films decreased with increase in ascorbic acid content. The oxygen permeability values were <ul style="list-style-type: none"> 0 M - 200 cm³ μm/m².d.kPa 0.05 M - 175 cm³ μm/m².d.kPa 0.1 M - 160 cm³ μm/m².d.kPa 0.2 M - 140 cm³ μm/m².d.kPa 	Janjarasskul, Tananuwong, and Krochta (2011)
Ascorbic acid + Whey protein isolate film	<ul style="list-style-type: none"> The ascorbic acid content in the films with varying amount of water activity (a_w) decreased from 250 mg/g of film to <ul style="list-style-type: none"> 230 mg/g - 0.25 (a_w) 220 mg/g - 0.5 (a_w) 200 mg/g - 0.7 (a_w) 100 mg/g - 0.95 (a_w) The ascorbic acid content in the films with varying pH decreased from 250 mg/g of film to <ul style="list-style-type: none"> 190 mg/g - 3 120 mg/g - 4.6 10 mg/g - 7.4 	Janjarasskul et al. (2013)
Ascorbic acid + (Iron/Zinc) + LLDPE	<ul style="list-style-type: none"> The oxygen scavenging capacity <ul style="list-style-type: none"> ascorbic acid + iron- 47.6 ml of O₂ in 750 h ascorbic acid + zinc- 37.4 ml of O₂ in 750 h. Food Sample used: Bread and Bun. The CFU/g of microbes for bun was <ul style="list-style-type: none"> No packaging - 70 ascorbic acid + iron-10 ascorbic acid + zinc-0 The CFU/g of microbes for bread was <ul style="list-style-type: none"> No packaging - 400 ascorbic acid + iron-41 ascorbic acid + zinc-40 	Matche, Sreekumar, and Raj (2011)

matrix is an interesting approach due to its environment friendly and inexpensive nature. Dried yeast immobilized in solid wax, paraffin or cloth has been used as a food grade oxygen scavenger (Nezat, 1985) (Edens, Ligtoet, & Van Der Plaat, 1992). The yeast when moistened with various media like water or ascorbic acid is activated, which in turn consumes oxygen for respiration (Nezat, 1985). When the technology was used for packaging of beer, it was found that the oxygen content reduced from 1.8 ppm to 1.2 ppm in 19 days for 40 mg yeast-wax where the wax to yeast ratio was 20:3 (Edens, Ligtoet, & Van Der Plaat, 1992).

Other aerobic microorganism like *Bacillus amyloliquefaciens*, *Kocuria varians* and *Pichia subpelliculosa* has also been used for oxygen scavenging purposes (Anthierens et al., 2011) (Altieri, Sinigaglia, Corbo, & Buonocore, 2004). It was found that it was possible to store the films for 20 days without any remarkable change in the microorganism viability (Altieri et al., 2004). This type of scavenging system is beneficial for high moisture containing food as the scavenging activity is initiated when water originating from the packaged food product is absorbed. The oxygen scavenging rate of *Bacillus amyloliquefaciens* immobilized on poly (ethylene terephthalate, 1,4-cyclohexane dimethanol) (PETG)

Table 6
Oxygen scavenging with enzymes in the active layer.

Oxygen scavenging active layer	Key Findings	Reference
Glucose oxidase + Catalase + latex	<ul style="list-style-type: none"> The activity of the enzymes decreased from 1.4 μmol O₂/min to 0.1 μmol O₂/min in 40 h due to the ageing of the enzymes. the scavenging rate with varying clay content <ul style="list-style-type: none"> 95 pph - 600 μmol O₂/min. g of substrate 33 pph - 450 μmol O₂/min. g of substrate 	Johansson et al. (2011)
Glucose oxidase and Catalase + LDPE	<ul style="list-style-type: none"> The industrial laminate with best scavenging capacity was found to be 7.6 ± 1.0 l/m². 	Andersson et al. (2002)
Oxalate oxidase + catalase + polymer	<ul style="list-style-type: none"> The addition of oxalic acid did not affect the enzyme activity substantially. <ul style="list-style-type: none"> Activity in presence of oxalic acid- 0.045 ± 0.017 μmol O₂/min. mg enzyme Activity in absence of oxalic acid- 0.045 ± 0.008 μmol O₂/min. mg enzyme The activity of the enzyme retained after immobilization depended on the substrate. <ul style="list-style-type: none"> 47.5% activity - PDMS silicone substrate 67% activity - PVC substrate 	Winestrand et al. (2013)
Laccase + Lignosulfates + latex/starch films	<ul style="list-style-type: none"> The films started scavenging action after 3 days. This was a result of time required to reach required relative humidity Containers with relative humidity less than 84% showed no scavenging activity. The oxygen concentration decreased from 1% to 0.3% in 6 days in the container with 100% relative humidity. 	Johansson, Winestrand, Johansson, Järnström, and Jönsson (2012)

was determined to be $0.10 \pm 0.02 \text{ ml O}_2 \text{ g}^{-1} \text{ PETG day}^{-1}$ (Anthierens et al., 2011).

2.8. Other scavenging systems

A technique of oxygen scavenging involves excitation of an organic or inorganic compound embedded in polymeric matrix by UV radiation (Rooney, 2002) (Zerdin, Rooney, & Vermuë, 2003). The compound gets excited to a higher energy state on excitation, which then reduces to a stable state. It does so by gaining or abstracting an electron or hydrogen atom or by redistributing them. The reduced state attained reacts with oxygen to produce hydrogen peroxide, hydroperoxyl radical or superoxide radical. 2-methylhydroquinone and 2-vinylanthraquinone are two organic compounds which when excited under UV radiation is known to act as an oxygen scavenger. An oxygen scavenging composition containing 2-methylhydroquinone, triphenylphosphine and ethyl cellulose reduced oxygen in headspace of a container from 14.6 vol% to 0.07 vol% in 25.3 h. The triphenylphosphine added scavenged the hydrogen peroxide formed in the due process (Rooney, 2002).

Other scavenging techniques use naturally occurring substances. Phenolic acids like gallic acid and salicylic acids are bio-based oxygen scavengers used for packaging food with high moisture content as the scavengers activate on contact with moisture. Sodium ascorbate is added along with gallic acid as it needs an alkaline medium to scavenge oxygen (Pant, Sangerlaub, & Muller, 2017). suggested that a polymeric film along with gallic acid exhibited a scavenging capacity of 470 mg O_2/g of gallic acid in 4 days. Similarly salicylic acid transition metal chelates along with an ascorbate compound showed a scavenging rate of 0.457 ppm O_2/g in 27 h (Zenner, Teumac, Deardurff, & Ross, 1994). Hydrotalcite is a naturally occurring mineral which acts as an active material for oxygen scavenging. It can scavenge oxygen up to 11.04 ppm O_2/g .day (Hallock & Speer, 1999). Apple pomace is another naturally occurring oxygen scavenger which has been used for storage of soyabean oil by increasing phenolic content in the films which were responsible for scavenging actions. It was observed that there was no significant lipid peroxidation of soyabean oil preserved with apple pomace films where those preserved with no films showed lipid peroxidation after 3 days (Gaikwad, Lee, & Lee, 2016). Another natural phenolic compound pyrogallol along with sodium carbonate was used for scavenging of oxygen. The headspace oxygen reduced from 21.1 vol % to 0.26 vol% in 8 days with a scavenging rate of 6.48 ml O_2/g .day. The scavenging capacity increased with increase in relative humidity and temperature (Gaikwad & Lee, 2016) (Gaikwad & Lee, 2017). Sodium erythorbate incorporated activated carbon was used by as oxygen scavenging agent by Joven, Garcia, Arias, and Medina (2015). The active packaging system scavenged 3.57 mg of O_2 in 11 days.

Some of the commercially available oxygen scavengers are mentioned in Table 7.

Table 7
Commercial oxygen scavengers.

Manufacturer	Commercial name	Scavenger	Product form
Albis	Shelfplus O_2	Iron based	Film
Aptar CSP Technologies	Activ-Film	UV activated scavenger -	Film
Bioka Ltd.	Bioka	Enzyme based-	Sachet/Laminates
BP Amoco Chemicals	Amosorb 3000	Photosensitive dye	Film
Clariant Ltd.	Oxy-Guard		Sachet
CMB Technologies	OXBAR	Cobalt Catalyst	Plastic bottle
Dessicare Ltd.	O-Buster	Iron powder + Zeolites	Sachet
Kyodo Printing Co. Ltd.	Oxy-Catch	Cerium oxide	Sachet
Laboratories Standa	ATCO	Iron/Organic based	Label
Mitsubishi Gas Chemical	AGELESS	Iron/Non-Iron based	Sachet/Label
Multisorb Technologies, Inc	Fresh Max, Fresh Pax	Iron	Sachet/Label
Sealed Air Food Care	Cryovac OS Film	UV activated scavenger	Film
Visy Industries	ZERO ₂	Photosensitive dye	Film
W.R. Grace & Co.	Darex	Ascorbate/Sulphite	Bottle Crown/Bottle

3. Conclusion

Over the years an extensive research has been done on developing oxygen scavenging system for food preserving application. This review highlights the major technologies used in the above mentioned field. The systems with high oxygen scavenging rate include iron, palladium and unsaturated hydrocarbon based scavengers. Nanoiron can be used both in presence of moisture or anhydrous environment and has scavenging rate as high as 60 cm^3 of $\text{O}_2 \text{ day}^{-1} \text{ g}^{-1}$ or reduces oxygen from 20.95 vol% to 9.45 vol% in 1 day. Palladium acts as a catalyst and converts oxygen to water in presence of hydrogen. These systems exhibit very high scavenging rate; oxygen content decreased from 2 vol% to 0.47 vol% in 2 min. At the same time this scavenging system needs a modified atmosphere with hydrogen present in it. Unsaturated hydrocarbon based scavenging systems are excellent option for dry foods but the formation of by-products like aldehydes, ketones or organic acids may affect the sensory quality of food. This problem is addressed by addition of a barrier layer which prevents the migration of the by-products. Also these systems need to be triggered by transition metal catalysts or UV radiation, but the scavenging rate can be as high as 450 cm^3 of $\text{O}_2 \text{ day}^{-1} \text{ g}^{-1}$. Other than the above mentioned chemical oxygen scavenging systems, the environment friendly systems like ascorbic acid, tocopherol, enzyme and microorganism based scavenging systems have slower scavenging rates. Ascorbic acid and α -tocopherol are the natural form of vitamin C and vitamin E found, hence are highly compatible for food packaging options. However, both the systems need to be triggered by light, UV, heat or transition metals and hence recur higher cost as compared to scavengers based on nanoiron. Tocopherol based systems are found to have scavenging rate of 0.21 cm^3 of $\text{O}_2 \text{ day}^{-1} \text{ g}^{-1}$ while that in ascorbic based systems can have scavenging rate of 11.9 cm^3 of $\text{O}_2 \text{ day}^{-1} \text{ g}^{-1}$. Enzyme based systems like glucose oxidase or oxalate oxidase produce hydrogen peroxide and hence require the enzyme catalase to convert it into water. These systems are highly prone to denaturation on exposure to temperature change, acid environment or on storage. Glucose oxidase based systems have been found to have scavenging rate of 15 cm^3 of $\text{O}_2 \text{ day}^{-1} \text{ g}^{-1}$. Microorganism based systems are inexpensive but are labile to temperature changes. Also introduction of microorganisms can lead to uncontrolled growth which can affect the sensory qualities of the food; this problem can be addressed by proper immobilization of the microorganisms so that they can't migrate. The scavenging rates are found to be 0.1 cm^3 of $\text{O}_2 \text{ day}^{-1} \text{ g}^{-1}$. Although environment friendly oxygen scavengers like ascorbic acid and tocopherol seem to be a promising solution for increasing shelf life and avoiding lipid oxidation in some food with low moisture content, it might be not be equally effective for foods with large dissolved oxygen present. An oxygen reduction up to 98% inhibited lipid oxidation to some extent (Johnson, Gisder, Lew, Goddard, & Decker, 2017). Furthermore, maintaining the pH of foods

below 4.6 facilitates eradication of botulism as *C. Botulinum* which is responsible for botulism does not grow at acidic pH (Lalitha & Gopakumar, 2005) (Lund, Graham, & Franklin, 1987).

Zero valent copper nanoparticles has not much been explored in the field of oxygen scavenging but has a great potential as an oxygen scavenger due to its easy oxidizable property. Also copper has antibacterial properties which is an added advantage in food packaging application.

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