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Innovative Development and Validation of Nanomaterials as Ethylene Adsorbers to Extend the Shelf-Life of Horticultural Commodities

PhD Program in Advanced Techniques for Research and Development in Food and Agriculture

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Cartagena (2021)

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INNOVATIVE DEVELOPMENT AND VALIDATION OF NANOMATERIALS AS ETHYLENE ADSORBERS TO EXTEND THE SHELF-LIFE OF HORTICULTURAL COMMODITIES

By

MARIANELA HAZEL ÁLVAREZ-HERNÁNDEZ

A dissertation submitted in partial fulfilment of the requirements for the degree of

DOCTOR OF PHILOSOPHY IN ADVANCED TECHNIQUES FOR RESEARCH AND DEVELOPMENT IN FOOD AND AGRICULTURE

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“Life is not easy for any of us. But what of that? We must have perseverance and above all confidence in ourselves. We must believe that we are gifted for something and that this thing must be attained.”

— Maria Salomea Skłodowska-Curie

DEDICATION

I dedicate this thesis to my grandparents ***Eusebia Méndez-Silverio and Jorge Hernández-Norberto*** for giving me their unconditional love, holding my hand since I was a baby and never letting me fall. Thank you for letting me fly, supporting me in my decisions and being my strength. You taught me that nothing is impossible.

I am who I am, and I am where I am because of you. That is why my achievements, more than being mine, are yours!

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TABLE OF CONTENTS

Page

LIST OF TABLES

Page

LIST OF FIGURES

Page

ABSTRACT

This PhD Thesis aimed to provide alternative tools to extend the shelf-life of horticultural commodities, preserving their physicochemical and sensory qualities. Particularly, we firstly focused on the development of $KMnO_4$-based C_2H_4 scavenging sachets for active packaging of fresh fruit. To improve the C_2H_4 removal activity of $KMnO_4$, the minerals sepiolite (SP) and montmorillonite (MMT) were chemically and physically treated to be used as $KMnO_4$ supports. The resulting materials were physicochemically characterized using X-ray diffraction, thermogravimetric analysis, transmission electron microscopy, scanning electron microscopy and nitrogen adsorption-desorption techniques. The results showed that protonation with HCl at a low concentration was effective in improving the surface properties of both SP and MMT, without damaging their structure. On the other hand, $KMnO_4$ was successfully incorporated by the two assayed clays, but the $KMnO_4$ loading process on SP resulted in a phase transformation. The $KMnO_4$-loaded acid-treated MMT revealed an C_2H_4 removal capacity of 10.16 mL g^{-1} at 22 °C, while the $KMnO_4$-loaded acid-treated SP (hereafter denoted as SK) revealed a capacity of 9.82 mL g^{-1}.

Subsequently, the obtained modified clays were incorporated into packages containing blueberry, apricot or cherry tomato fruit in order to be validated. Fruit packed without C_2H_4 scavengers were used as controls. The effect of the modified clays was evaluated on the quality attributes of blueberries at 2 and 10 °C under modified atmosphere packaging (MAP); apricots at 2 and 15 °C under MAP and air packaging conditions, respectively; and tomatoes at 11 °C + 3 days at 22 °C (simulation of commercialization at 22 ºC) under air packaging conditions. Weight loss, fruit firmness, skin colour, total soluble solids content (SSC), titratable acidity (TA), pH, microbiological quality and sensory parameters were monitored during storage. According to the results, both modified clays were efficient to reduce in-package C_2H_4 concentrations generated by the plant products. The modified MMT extended the blueberry shelf-life by reducing the fungal incidence, while the rest of the quality attributes were not affected. In apricots, the SK allowed less weight loss, TA decrease, SSC/TA ratio increase, and fungal incidence, while maintained the highest sensory quality. Moreover, the 15 °C–stored apricots also showed less pH and higher C* colour coordinate, as well as reduced SSC changes. In cherry tomato, SK resulted in a delayed weight loss, without disturbing the other monitored quality parameters. The effect of combining SK and thymol was further assayed in cherry tomatoes. SK was shown to be as good as thymol in reducing grey mould but using them together can induce the fruit susceptibility to *Botrytis cinerea*. Conclusively, the developed C_2H_4 scavengers have great potential in active packaging of fresh horticultural produce.

RESUMEN

El objetivo de esta tesis doctoral fue proporcionar herramientas alternativas para extender la vida útil de productos hortofrutícolas, preservando sus cualidades fisicoquímicas y sensoriales. Particularmente, nos enfocamos en el desarrollo de *sachets* de eliminación de C_2H_4 a base de $KMnO_4$ para el envasado activo de productos hortofrutícolas frescos. Para optimizar la eliminación de C_2H_4 mediante $KMnO_4$, se trataron las arcillas sepiolita (SP) y montmorillonita (MMT) química y físicamente para usarlas como soportes del material adsorbente. Los materiales resultantes se caracterizaron mediante difracción de rayos X, análisis termogravimétrico, microscopía electrónica de transmisión y de barrido, y técnicas de adsorción-desorción de nitrógeno. Los resultados mostraron que la protonación con HCl a baja concentración mejoró las propiedades superficiales de ambas arcillas, sin dañar su estructura. El $KMnO_4$ fue satisfactoriamente incorporado en las dos arcillas, pero el proceso de carga de $KMnO_4$ en SP dio lugar a una transformación de fase. La MMT tratada con ácido y cargada con $KMnO_4$ reveló una capacidad de eliminación de C_2H_4 de 10.16 mL g^{-1} a 22 °C, mientras que la SP cargada con $KMnO_4$ (de aquí en adelante denotada como SK) mostró una capacidad de 9.82 mL g^{-1}.

Posteriormente, las arcillas obtenidas se incorporaron en envases que contenían frutos de arándano, albaricoque o tomate cherry. Como control se utilizaron productos envasados sin adsorbedores de C_2H_4. Se evaluó el efecto de las arcillas modificadas en arándanos a 2 y 10 °C bajo envasado en atmósfera modificada (MAP); albaricoques a 2 y 15 °C en condiciones de MAP y envasado en aire ambiente, respectivamente; y tomates a 11 °C + 3 días a 22 °C en envasado en aire ambiente. Durante el almacenamiento se registró la pérdida de peso, firmeza, contenido de sólidos solubles totales (SSC), color, acidez titulable (TA), pH, calidad microbiológica y parámetros sensoriales. Según los resultados, ambas arcillas modificadas fueron eficaces en reducir las concentraciones de C_2H_4 en los envases. La MMT modificada extendió la vida útil del arándano reduciendo la incidencia de hongo, sin afectar los atributos restantes. En los albaricoques, SK disminuyó los cambios en peso, TA, SSC/TA e incidencia de hongos, mostrando la calidad sensorial más alta. Los albaricoques almacenados a 15 °C mostraron menor aumento en los valores de C* y pH, así como reducidos cambios de SSC. En tomate, SK llevó a menor pérdida de peso, sin alterar los otros parámetros. El efecto de combinar SK y timol se ensayó adicionalmente en tomates cherry. Se demostró que SK es tan bueno como el timol para reducir el moho gris, pero usarlos juntos puede incrementar la susceptibilidad de la fruta a *Botrytis cinerea*. En conclusión, los adsorbedores de C_2H_4 desarrollados tienen un gran potencial en el envasado activo de productos hortofrutícolas frescos.

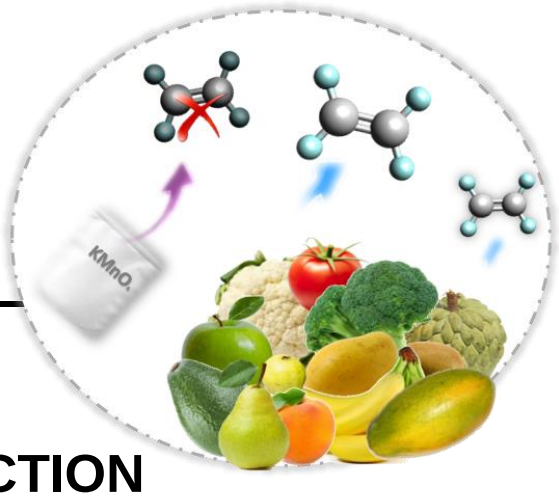
LIST OF ABBREVIATIONS AND ACRONYMS

°C	Degree Celsius
µL	Microlitre(s)
µm	Micrometre(s)
Å	Angstrom(s)
ACC	1-aminocyclopropane-1-carboxylic acid
AcMt	Montmorillonite swelled in water and treated with HCl
AcMt+$KMnO_4$	AcMt impregnated with $KMnO_4$-solution
ACO	ACC oxidase
ACS	1-aminocyclopropane-1-carboxylase synthase
Adj. R^2	Adjusted coefficient of determination
AHP	Histidine-containing phosphotransferase proteins in *Arabidopsis*
AIR	Air packaging atmosphere
AIR+COM_{BION}	Air packaging atmosphere along with the commercial scavenger Bion R-12
AIR+SK	Air packaging atmosphere along with $KMnO_4$-loaded protonated sepiolite
ANOVA	Analysis of variance
ARR	Response regulator proteins in *Arabidopsis*
ATP	Adenosine triphosphate
BET	Brunauer-Emmett-Teller
BOPP	Bioriented polypropylene
CFU	Colony-forming unit
CI	Colour index
CIE	Comission Internationale de l´Eclairage
cmol	Centimole(s)
COL	Tomato colour index
COM	Commercial $KMnO_4$-based ethylene scavenger
CTR1	Constitutive triple response1
CTRL	Control de evaluation
d_{001}	Basal plane spacing
DI	Decay index
DTG	Derivative thermogravimetry
EBF 1/2	EIN3-binding F-box 1 and EIN3-binding F-box 2
EIL1	EIN3 and EIN3-LIKE1
EIL2	Ethylene insensitive 3-like 2 protein
EIN2	Ethylene insensitive 2
EIN2-C	C-terminal portion of EIN2

EIN2-N	Membrane-bound N-terminal
EIN3	Ethylene insensitive 3
EIN4	Ethylene insensitive 4
EIN5	Ethylene insensitive 5
ENAP1	EIN2 nuclear associated protein 1
EOs	Essential oils
EPA	Environmental Protection Agency
ER	Endoplasmic reticulum
ERR	Ethylene removal rate
ERS1	Ethylene response sensor 1
ERS2	Ethylene response sensor 2
ET	Encapsulated thymol
ETP 1/2	EIN2-targeting protein 1/2
ETR1	Ethylene response 1
ETR2	Ethylene response 2
EU	European Union
FDA	Food and Drug Administration
FE-SEM	Field emission-Scanning electron microscopy
FID	Flame ionization detector
GC	Gas chromatography
GHS	Globally Harmonized System
HDPE	High-density polyethylene
HLB	Hydrophilic–lipophilic balance
ICDD	International Centre for Diffraction Data
IU	International units
IUPAC	International Union of Pure and Applied Chemistry
K	Kelvin
kg	Kilogram(s)
kV	Kilovolt(s)
L	Litre(s)
LD50	Median lethal dose
LSD	Least significant difference
LU	Limit of usability
M	Molar
mA	Milliampere(s)
MACC	Malonyl-ACC
MAP	Modified atmosphere packaging
MAP+COM_{BION}	MAP along with the commercial scavenger Bion R-12
MAP+COM_{BION}	MAP along with the commercial scavenger Bion R-12
MAP+PMMT	MAP along with $KMnO_4$-loaded protonated montmorillonite

MAP+SK	MAP along with $KMnO_4$-loaded protonated sepiolite
meq	Milliequivalent(s)
MI	Maturity index
mL	Millilitre(s)
mm	Millimetre(s)
MMT	Montmorillonite
mRNA	Messenger ribonucleic acid
Mt+$KMnO_4$	Dry blend of montmorillonite and $KMnO_4$
MTA	5’-methylthioadenosine
N	Newton(s)
nL	Nanolitre(s)
nm	nanometre(s)
nmol	Nanomole(s)
P-body	Cytoplasmic processing-body
PDA	Potato dextrose agar
PE	Polyethylene
Pi	Inorganic phosphate
pmol	Picomole(s)
PP	Polypropylene
PPi	Inorganic pyrophosphate
ppm	Parts per million
Pristine Mt	No treated montmorillonite
R^2	Coefficient of determination
RAN1	Responsive to antagonist 1
RH	Relative humidity
RMSE	Root mean squared error
ROS	Reactive oxygen species
rpm	Revolutions per minute
RR	Respiration rate
S-AdoMet	S-adenosylmethionine
SAM	S-adenosyl-L-methionine
SCF-E3	Skp1 Cullen F-box E3 ubiquitin ligase complex
SEM	Scanning electron microscopy
SK	$KMnO_4$-loaded acidic-treated sepiolite
SK	$KMnO_4$-loaded sepiolite
SK+0.04ET	$KMnO_4$-loaded acidic-treated sepiolite plus encapsulated thymol
SP	Sepiolite
SSC	Total soluble solids content
SSE	Sum of squared errors

SwMt	Montmorillonite swelled in water
SwMt+$KMnO_4$	SwMt impregnated with $KMnO_4$-solution
T	Non-encapsulated thymol
TA	Titratable acidity
TCD	Thermal conductivity detector
TEM	Transmission electron microscopy
TG	Thermogravimetric
TPP	Sodium tripolyphosphate
USA	United States of America
UV	Ultraviolet
UV-B	Ultraviolet B rays
v/v	Volume/volume
VUV	Vacuum ultraviolet
w/v	Weight/volume
w/w	Weight/weight
WAXS	Wide-angle X-ray scattering
WDXRF	Wavelength dispersive X-ray fluorescence
WHO	World Health Organization
XRD	X-ray diffraction
Y+M	Yeast and moulds sum
ΔE*	Total colour differences



INTRODUCTION

1 ETHYLENE IN POSTHARVEST TECHNOLOGY

1.1 Ethylene biochemistry

The C_2H_4, ethene (IUPAC), is a colourless gaseous hydrocarbon made up of two carbon atoms linked by a double bond (Figure 1), being the simplest alkene (NCBI, 2021). Besides being one of the most widely anthropogenically produced and industrially utilized organic compounds worldwide (Li et al., 2018). The compound C_2H_4 is also a naturally occurring plant hormone (phytohormone). It is synthesized in practically all parts of higher plants and easily diffuses inside the plant through intercellular spaces due to its gaseous nature (Botton et al., 2019).

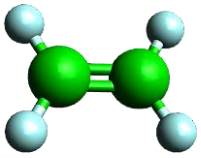


Figure 1. Ethylene molecule (source: Own elaboration).

The gas C_2H_4 is involved in several processes of plant growth and development, including seed germination, fruit ripening and senescence, leaf and flower abscission, interaction with pathogens, responses to stress, and other physiological functions (Abeles et al., 1992; Koenig et al., 2020). However, due to commercial and social interests, C_2H_4 research is especially focused on postharvest physiology. As molecular and biochemical techniques have advanced, the understanding of C_2H_4 biosynthesis, perception and signal transduction has increased. This knowledge has been used to regulate C_2H_4 production and response and then, to enhance the quality of several agricultural commodities.

1.1.1 Biosynthesis of ethylene in fruit and vegetables

The C_2H_4 biosynthetic pathway is known as the Yang's cycle because the Taiwanese-American plant scientist Dr. Shang Fa Yang significantly contributed to its elucidation carrying out several studies (as reviewed in Bradford (2008)). In general terms, the pathway of C_2H_4 biosynthesis is formed by two key steps: the conversion of SAM to ACC and then, the conversion of ACC to C_2H_4 (Figure 2). The first step is carried out by the enzyme ACS through a β,γ carbon elimination reaction (Argueso et al., 2007), producing also 5'-methylthioadenosine (Wang et al., 2002). Subsequently, in the presence of O_2, the enzyme ACO modifies the carbons C-2 and C-3 of ACC to give rise to C_2H_4, whereas C-1 is transformed into cyanide and the carboxyl group is converted into cyanide (Argueso et al., 2007).

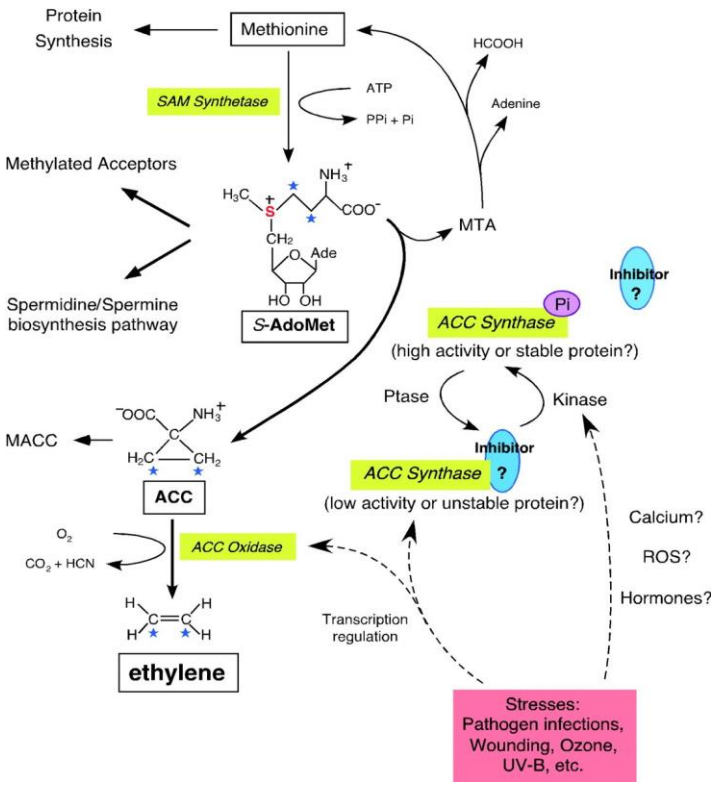


Figure 2. Biosynthetic pathway of ethylene. SAM: S-adenosyl-L-methionine; ATP: Adenosine triphosphate; PPi: Inorganic pyrophosphate; Pi: Inorganic phosphate; MTA: 5'-methylthioadenosine; S-AdoMet: S-adenosylmethionine; ACC: 1-aminocyclopropane-1-carboxylic acid; MACC: Malonyl-ACC; ROS: Reactive oxygen species; UV-B: Ultraviolet B rays (source: Wang et al. (2002)).

The C_2H_4 precursor SAM is synthesized by the enzyme S-adenosyl-methionine synthase from the amino acid methionine and ATP (Lieberman et al., 1965; Yang et al., 1966). Meanwhile, the methylthio group and the ribose moiety from the methylthioadenosine resulting from SAM catalysis are recycled to generate methionine, maintaining a constant level of such amino acid while the C_2H_4 production rate is increased (Wang et al., 2002). The ATP required for such methionine cycle is obtained by increased respiration (Barry & Giovannoni, 2007).

Multiple regulation points are involved in the C_2H_4 synthesis, being regulated by internal signals and environmental stimuli (Wang et al., 2002). In addition to O_2, the presence of light, CO_2, O_2, and H_2O stress affect the conversion of ACC to C_2H_4 (Bradford, 2008). Moreover, the conversion of ACC to C_2H_4 is stereospecific and can be inhibited by the L-forms of alanine and methionine (Hoffman et al., 1982). On the other hand, ACC may be conjugated into malonyl-ACC (formed by ACC N-malonyl transferase enzyme), γ-glutamyl-ACC (formed by γ-glutamyl-transpeptidase) or jasmonyl-AC (reviewed in de Poel & Van Der Straeten (2014)), becoming unsuitable for transformation into C_2H_4. Naturally, the transcription control of ACS and ACO genes determines the activation state and stability of

the corresponding encoded enzymes and then, the final levels of C_2H_4 (Barry & Giovannoni, 2007). Both ACS and ACO enzymes are encoded by multigene families that are regulated by biotic and abiotic factors (Wang et al., 2002). Particularly, the enzyme ACS acts as a dimer and is believed to catalyse the rate-limiting step of C_2H_4 biosynthesis (Botton et al., 2018; Wang et al., 2002). However, it has been proved that ACO can be a rate-limiting step controlling C_2H_4 production during certain processes (reviewed in Houben & Van de Poel (2019)).

The highest C_2H_4 biosynthesis occurs during the climacteric rise of fruit and plant tissues undergoing senescence (Argueso et al., 2007). Climacteric fruit (and fruit vegetables) are those whose ripening is associated with a pronounced rise in the respiration rate (RR) and a concomitant increment in C_2H_4 production (i.e. C_2H_4/respiratory climacteric) (Barry & Giovannoni, 2007). In contrast, non-climacteric fruit keeps its CO_2 and C_2H_4 production at basal levels during ripening (Brizzolara et al., 2020). All plant tissues can produce high C_2H_4 rates in response to stress, but only climacteric fruits do so normally during their development (Brecht, 2019). During ripening or senescence of climacteric crops, C_2H_4 behaviour changes from autoinhibitory to autocatalytic by the upregulation of a high catalytic and stable ACS, which results from kinase-mediated phosphorylation (Fernandez-Moreno & Stepanova, 2020). The latter leads to the climacteric burst and induces the expression of ripening-associated genes (Barry & Giovannoni, 2007; Botton et al., 2019). Meanwhile, the inhibition of C_2H_4 biosynthesis is due to ACS ubiquitination, resulting from phosphatase-mediated dephosphorylation (Fernandez-Moreno & Stepanova, 2020). The autoinhibitory mode of C_2H_4 biosynthesis is known as 'system 1' and works releasing basal C_2H_4 levels during plant growth and development, as well as during stress conditions (Barry & Giovannoni, 2007). In contrast, the autocatalytic mode is known as 'system 2', and the climacteric C_2H_4 production is attributed to it.

On the other hand, C_2H_4 biosynthesis can also be regulated by crosstalk with other hormones during postharvest (as reviewed by Botton et al. (2018)). For instance, the sprayed application of auxins (e.g. the synthetic auxins NAA or 2,4D) after the onset of fruit ripening, may lead to the enhancement of ripening through the increased transcription of ACS-encoding genes and in consequence to the C_2H_4 synthesis. The exogenous abscisic acid application also leads to enhanced C_2H_4 production. The pre-ripening application of cytokinins reduces C_2H_4 biosynthesis and sensitivity, as well as the respiration climacteric rise, while the application after the ripening onset may result in a contrary effect. The application of postharvest gibberellins and polyamines sprays has been reported to downregulate C_2H_4 biosynthesis and sensitivity, enhancing fruit firmness suppressing cell

wall enzymes. Meanwhile, nitric oxide downregulates C_2H_4 synthesis by inhibiting the transcription and activity of the ACS and ACO enzymes through protein S-nitrosylation.

1.1.2 Ethylene perception and signalling in fruit and vegetables

Once the C_2H_4 has been synthetized, the active hormone is then perceived by the same cell, solubilizes and diffuses across the membranes to neighbouring cells and beyond (Fernandez-Moreno & Stepanova, 2020). Specifically, C_2H_4 is perceived by a family of receptors related to prokaryotic two-component histidine kinases and located at the endoplasmic reticulum, with the C_2H_4 binding site within the membrane (Botton et al., 2019). The C_2H_4 binding requires a copper ion cofactor, which is provided by the Golgi-localized protein RAN1 (Fernandez-Moreno & Stepanova, 2020). Considering the differences that may exist between climacteric and non-climacteric fruits, Chen et al. (2018) compared their C_2H_4 receptors and related membrane-localized proteins. The last authors found only two remarkable differences: climacteric fruit seems to posse a higher number of C_2H_4 receptor genes than non-climacteric fruit, while this last fruit type may have an earlier C_2H_4 receptor expression peak relative to sugar accumulation.

The major target of the C_2H_4 receptors is the CTR1 Ser/Thr kinase, which is related to the eukaryote-specific protein family (Azhar et al., 2020). CTR1 is a negative regulator that, in the absence of C_2H_4, represses C_2H_4 responses by phosphorylating the C-terminus of EIN2 transmembrane protein —a positive regulator related to eukaryote-specific protein families—, which is then degraded through the proteasome (Figure 3; Binder (2020)). The CTR1 is inactivated when C_2H_4 binds to receptors, allowing C_2H_4 responses to proceed (Brecht, 2019). Then, in the presence of C_2H_4, the EIN2 C-terminus migrates from the endoplasmic reticulum to the nucleus, where the plant-specific EIL1 transcription factors are potentiated to trigger transcriptional C_2H_4 responses (Azhar et al., 2020). The levels of EIN3 and EIL1 are controlled by the F-box proteins EBF1/2 that, in the absence of C_2H_4, degrades these factors via a proteasome-dependent mechanism (Azhar et al., 2020). In the presence of C_2H_4, the two F-boxes proteins can be proteolyzed themselves, leading to the accumulation of EIN3 and EIL1 (Barry & Giovannoni, 2007). Nevertheless, the EIN2 C-terminus may migrate to cytoplasmic P-bodies where, in conjunction with the exoribonuclease EIN5, it can inhibit the translation of the two F-box protein mRNAs (Barry & Giovannoni, 2007; Fernandez-Moreno & Stepanova, 2020). When the C_2H_4 signal ceases, the two F-boxes proteins are synthetized and turnover the EIN3 and EIL1 transcription factors, stopping C_2H_4 responses (Binder, 2020).

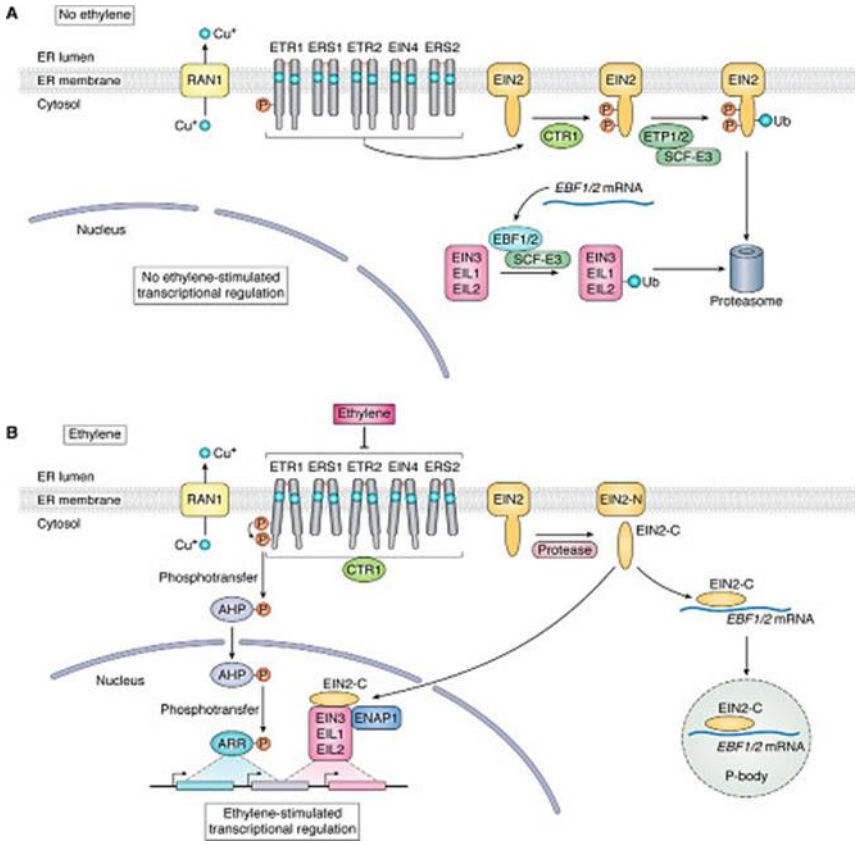


Figure 3. Model for ethylene signal transduction. ER: Endoplasmic reticulum; RAN1: Responsive to antagonist 1; ETR1: Ethylene response 1; ERS1: Ethylene response sensor 1; ETR2: Ethylene response 2; EIN4: Ethylene insensitive 4; ERS2: Ethylene response sensor 2; EIN2: Ethylene insensitive 2; CTR1: Constitutive triple response1; ETP1/2: EIN2-targeting protein 1/2; SCF-E3: Skp1 Cullen F-box E3 ubiquitin ligase complex; EBF1/2: EIN3-binding F-box 1 and EIN3-binding F-box 2; mRNA: Messenger ribonucleic acid; EIN3: Ethylene insensitive 3; EIL1: EIN3 and EIN3-LIKE1; EIL2: Ethylene insensitive 3-like 2 protein; EIN2-N: Membrane-bound N-terminal; EIN2-C: C-terminal portion of EIN2; AHP: Histidine-containing phosphotransferase proteins in Arabidopsi; ARR: Response regulator proteins in Arabidopsis; ENAP1: EIN2 nuclear associated protein 1; P-body: Cytoplasmic processing-body (source: Binder (2020)).

One of the responses to C_2H_4 is an increased activity of ACS enzyme resulting in autocatalytic C_2H_4 production, as mentioned in the previous section. Thus, any increase in C_2H_4 synthesis can trigger pronounced endogenous C_2H_4 upsurges. Since C_2H_4 is diffused from one site to another, its effects are usually regulated by its synthesis rate. Nevertheless, when C_2H_4 biosynthesis is autocatalytic, the C_2H_4 presence can trigger the C_2H_4 production or responses in neighbouring plant organs, including neighbouring crops such as in storage rooms (Brecht, 2019). In addition, plant tissues can respond to C_2H_4 coming from microbial production and anthropogenic sources such as hydrocarbon combustion (e.g. gases from internal combustion engines/heaters), air pollution (coal combustion, oil, natural gas, or biomass), smoke, welding and natural gas leaks (Keller et al., 2013).

1.2 Ethylene effects on the fresh produce quality

All horticultural products respond to C_2H_4, but in a different way (Saltveit, 1999). When high C_2H_4 concentrations are applied in climacteric fruit, the emergence of the respiratory peak is accelerated, and the C_2H_4-dependent genes are upregulated, triggering the autocatalytic C_2H_4 production (Brizzolara et al., 2020). In contrast, in non-climacteric produce, the RR usually increases as the C_2H_4 concentration increases, but the timing of the respiration peak is not affected (Brizzolara et al., 2020). However, there are species in which the produce of different varieties and cultivars exhibit both climacteric and non-climacteric behaviour, such as melon and plums (Barry & Giovannoni, 2007).

During maturation, ripening and senescence, C_2H_4 triggers a chain of reactions in fruit and vegetables such as biosynthesis of pigments, aromas, and flavours, starch conversion into sugar, overexpression induction of chlorophyllase encoding genes and transcriptional activation of genes encoding enzymes involved in cell wall changes, resulting in changes in organoleptic and nutritional quality (Botton et al., 2019; Brecht, 2019). These changes can be considered beneficial or detrimental (Table 1), depending on human needs. Moreover, the same C_2H_4 response may be perceived as beneficial in some produce and damages in others (as early reviewed in Kader & Kasmire (1984), Saltveit (1999) and Watada (1986)).

Table 1. Summary of positive (desirable) and negative (undesirable) effects of C_2H_4 on the postharvest quality of fresh produce (source: Own elaboration).

Positive effects	Negative effects
Inhibits C_2H_4 synthesis in vegetative tissue and non-climacteric fruit.	Promotes C_2H_4 synthesis in climacteric fruit.
Uniform and accelerated ripening of climacteric fruit.	Accelerates senescence of plant tissues.
Stimulates dehiscence in nuts.	Enhances excessive fruit softening.
Promotes aroma development.	Promotes off-flavours.
Promotes colour development in fruit (e.g. de-greening of citrus and anthocyanin synthesis).	Promotes discolouration (e.g. chlorophyll breakdown-related yellowing and browning).
Increases sugar development.	Causes toughening (lignification) of vegetable.
Enhances defence against certain pathogens.	Stimulates sprouting of tubercles and bulbs.
Reduction of chilling injury in honeydew melon.	Increased sensitivity to chilling injury.
	Promotes phenylpropanoid metabolism (bitter compounds, discolouration and browning).

For instance, de-greening of citrus and bananas; induction of pigment synthesis in apples and tomatoes; less chilling sensitivity of honeydew melons; accelerated ripening in tomato and melons; and induction of phenylpropanoid metabolism to increase defences against pathogens may be viewed as beneficial effects (Saltveit, 1999). Meanwhile, examples of negative effects include fresh produce decay and excessive softening; russet spotting development in eggplants and leafy vegetables such as lettuce; yellowing (i.e. chlorophyll breakdown) of green vegetables such as cucumbers, broccoli, and Brussel sprouts; internal browning of pear and peach; off-odour incidence in garlic and onions; bitter-tasting phenolic compounds synthesis in carrot, lettuce and parsnip roots; increased chilling sensitivity of avocado, persimmon and grapefruit; wilting of vegetables; scald and loss of crunch in apples; sprouting of potato and onion; hastened toughening (i.e. phenolic metabolism related to lignification of cell walls) of vegetables; and rind breakdown in citrus (Brecht, 2019; Keller et al., 2013; Watada, 1986). Then, when, for instance, an accelerated fruit colour development and a climacteric fruit ripening are desired, C_2H_4 can be added to the storage environment. However, when not desired, the C_2H_4 presence may accelerate produce deterioration shortening commercial- and shelf-life. The above is relevant when it comes to products destined for long-distance transport or that have to be stored for long periods, making C_2H_4 removal a necessity, as C_2H_4 may strongly affect the final quality of fresh produce.

2 ETHYLENE REMOVAL TECHNIQUES APPLIED IN POSTHARVEST TECHNOLOGY

Studies indicated that one-third of the food produced globally is lost (Porat et al., 2018). Particularly, it has been estimated that up to 60 % of the perishable horticultural commodities are lost and waste around the world (Yahia et al., 2019). Reducing food loss along production and supply chains and waste at the retail and consumer levels is considered an important way to streamline food system costs, enhance food security and contribute to environmental sustainability (FAO, 2019b). In addition, reducing food loss and waste is part of worldwide efforts against global hunger and improve nutrition (Porat et al., 2018). A large portion of food waste occurs during consumption (Figure 4), especially in developed countries (Porat et al., 2018). Therefore, proper postharvest handling techniques are of paramount importance to maintain high-quality produce from harvesting until consumption. Different studies have shown that ripening- and senescence-related metabolic processes may be delayed by reducing C_2H_4 concentrations in the surrounding atmosphere (compiled by Wills (2015)).

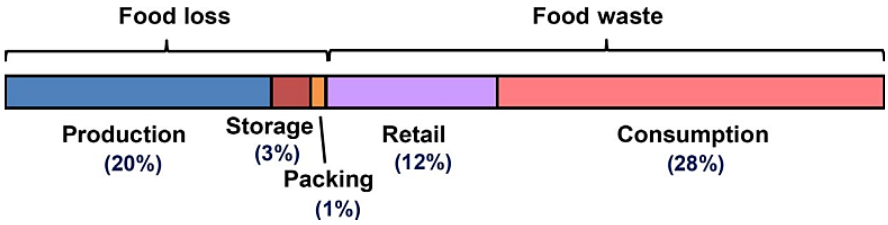


Figure 4. Food loss and waste percentages along the supply chain in Australia, Canada, New Zealand, and USA (source: Porat et al. (2018)).

One common way to avoid C_2H_4 accumulation inside storage facilities and transport vehicles/chambers is the use of adequate ventilation (Botton et al., 2019). With this aim, refrigeration systems are designed to exchange a certain amount of air between the conditioned space and the outside environment (Brecht, 2019). However, major drawbacks of this method are the need to cool and dehumidify the incoming ambient, possible outdoor air pollution with C_2H_4, and frequent defrosting requirement of the evaporator coils, which results in extra load on the refrigeration system, expensive costs and decreased ventilation efficiency due to presence in ambient air (Keller et al., 2013). Moreover, the air flow across produce can increase the produce H_2O loss (Wills & Golding, 2015). To further reduce the C_2H_4 concentration in the postharvest environment, C_2H_4 removal systems based on physical or/and chemical processes (Figure 5) are often applied (Awalgaonkar et al., 2020; Botton et al., 2019).

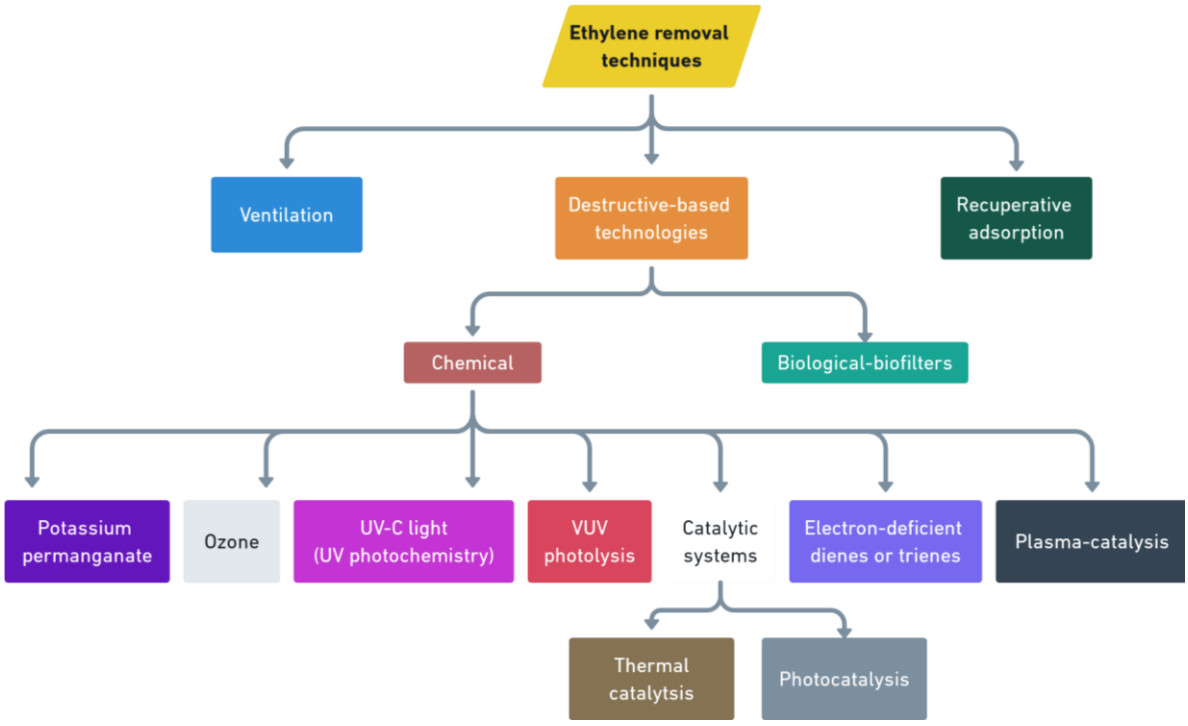


Figure 5. Main ethylene removal techniques to maintain postharvest fruit and vegetable quality (source: Own elaboration).

2.1 Ethylene adsorption-based technology

The easiest way to limit the C_2H_4 response of susceptible sensitive crops is the C_2H_4 adsorption from the storage and handling environment (Keller et al., 2013). This method exploits the ability of certain minerals to trap C_2H_4 directly from a fluid stream via adsorption mechanisms such as H_2 bonding interactions (CH-O interactions) (Brecht, 2019; Coloma et al., 2014). Current C_2H_4 scrubbing technologies include carbon-based materials, zeolites (e.g. chabazite, modernite, and clinoptilolite) —which not only adsorbs C_2H_4 but also absorbs it—, clays (e.g. montmorillonite (MMT) and halloysite nanotubes), palladium-based products, as reviewed elsewhere (Awalgaonkar et al., 2020; Gaikwad & Lee, 2017; Keller et al., 2013). In the case of silicate-based materials, the C_2H_4 adsorption process occurs through $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ structural tetrahedral units (Sadeghi et al., 2021). In addition to the aforementioned materials, metal-organic frameworks (metal ions, or ion clusters, bound to organic molecules, like metal exchanged zeolites) have been developed to bind C_2H_4 through C_2H_4 molecule and OH group interaction, as well as by interactions between C_2H_4 π–electrons and incorporated metal cations (Chopra et al., 2017; de Abreu et al., 2017).

The efficiency of adsorption-based tools depends on parameters such as temperature, adsorber quantity, morphological characteristics of the C_2H_4 adsorbing material, partial pressure and gaseous composition —particularly, the presence of molecules that can compete for adsorption sites — (Álvarez-Hernández et al., 2018; Awalgaonkar et al., 2020). For instance, in presence of moisture, zeolites decrease their C_2H_4 adsorption capacity because Si-OH-Al and Si-OH sites are blocked by H_2O molecules (Sadeghi et al., 2021). Moreover, under certain circumstances, the adsorbed C_2H_4 can be released from the sorption sites of the adsorbing material (Keller et al., 2013). Compared with C_2H_4 oxidative removal techniques, the adsorption-based tools are usually much less effective — although palladium has shown a higher C_2H_4 removal efficiency than the oxidative C_2H_4 agent permanganate (Gaikwad & Lee, 2017).

2.2 Ethylene destructive-based technologies

In contrast to the adsorption technology, which is a recuperative method, destructive technology allows continuous and irreversible C_2H_4 removal. In this sense, C_2H_4 can be chemically oxidated into CO_2 and H_2O in several ways including $KMnO_4$, O_3 and catalyst-based C_2H_4 scavengers systems (Brecht, 2019).

2.2.1 Potassium permanganate-based ethylene removal strategies

The oxidant $KMnO_4$ is the most popular agent to scavenge C_2H_4 during postharvest storage (Brecht, 2019). $KMnO_4$ has demonstrated the ability to remove C_2H_4 at different temperatures, including cold storage and ambient temperature (Álvarez-Hernández et al., 2019). According to Hu et al. (2019), the general stoichiometric oxidation reaction can be described as:

$$3C_2H_4 + 12KMnO_4 + 2H_2O \rightarrow 6CO_2 + 2H_2O + 12MnO_2 + 12KOH \quad (1)$$

Meanwhile, Keller et al. (2013) described the C_2H_4 stoichiometric oxidation reaction as follows:

$$3CH_2CH_2 + 2KMnO_4 + H_2O \rightarrow 2MnO_2 + 3CH_3CHO + 2KOH \quad (2)$$

$$3CH_3CHO + 2KMnO_4 + H_2O \rightarrow 3CH_3COOH + 2MnO_2 + 2KOH \quad (3)$$

$$3CH_3COOH + 8KMnO_4 \rightarrow 6CO_2 + 8MnO_2 + 8KOH + 2H_2O \quad (4)$$

To enhance the C_2H_4 oxidizing process, $KMnO_4$ is usually supported onto an inert porous C_2H_4 adsorbing material with small particle size and high surface area (e.g. activated alumina, silica gel, vermiculite, zeolite, among others; Álvarez-Hernández et al. (2018)). Since the $KMnO_4$ is rapidly consumed and the necessary $KMnO_4$ amount is related to the C_2H_4 fruit production, the $KMnO_4$-based C_2H_4 scavenging technology is appropriate for small storage amenities, including packaging systems (Pathak et al., 2019). In fact, most studies have examined the effect of $KMnO_4$-based C_2H_4 scavengers in conjunction with modified atmosphere packaging (i.e. active packaging), as reviewed in Álvarez-Hernández et al. (2019). One disadvantage of using $KMnO_4$-containing tools is that such tools sometimes have to be frequently replaced with a fresh supply (Keller et al., 2013).

2.2.2 Ozone-based ethylene oxidation

The powerful oxidant O_3 is usually generated from atmospheric O_2 employing a high energy input coming from electrochemical systems, UV radiation or corona (electrical) discharge, being the last method the most commonly used because it is the cheapest and achieves the best O_3 yields (Miller et al., 2013). According to Keller et al. (2013), the C_2H_4- O_3 reaction can be expressed as follows:

$$2O_3 + C_2H_4 \rightarrow 2CO_2 + 2H_2O \quad (5)$$

The higher the O_3 production rate, the higher C_2H_4 the reduction rate (as reviewed in Tzortzakis & Chrysargyris (2017)). However, O_3 is a quite unstable molecule and can cause severe and irreversible damage in both human and plant tissues (Miller et al., 2013). Therefore, O_3-generating systems have to be designed with a rigorous O_3 upper concentration limit or with an O_3 auto-reduction mechanism (Brecht, 2019).

2.2.3 UV light photochemically activated processes

Photochemistry by UV-C light (radiation at 184 and 254 nm) is useful to indirectly degrading C_2H_4 at temperatures below 100 °C, including ambient or even sub-ambient temperatures (Keller et al., 2013). Jozwiak et al. (2000) proposed a model describing the UV-initiated photochemical and chemical processes leading to C_2H_4 breakdown:

$$O_2 + h\nu\,(184.9\,nm) \rightarrow O + O \quad (6)$$

$$O_2 + O + inert\ third\ body \rightarrow O_3 + inert\ third\ body \quad (7)$$

$$O_3 + h\nu\,(253.7\,nm) \rightarrow O_2 + O \quad (8)$$

$$O_3 + O \rightarrow O_2 + O_2 \quad (9)$$

$$O + C_2H_4 \rightarrow products \quad (10)$$

$$O_3 + C_2H_4 \rightarrow products \quad (11)$$

Although the aforementioned UV-C_2H_4 remover systems did not significantly contribute to the heat load on cold storage and it has been found to require little energy, this system is generally useful for very low C_2H_4 concentrations (its efficiency is approximately 7 %; Lawton (1991)).

2.2.4 Vacuum ultraviolet light photolysis

The C_2H_4 removal under VUV photolysis systems consists of the $\pi \rightarrow \pi^*$ excitation (i.e. excitation of an electron in a conjugated π system to a π* orbital) using VUV radiation (at < 200 nm) and subsequent C_2H_4 photodissociation (Allison et al., 2012). Particularly, in the VUV C_2H_4 photodissociation, the O_2 and gaseous H_2O molecules are dissociated by VUV photons producing ROS, which eventually oxidise C_2H_4 (Pathak et al., 2019). Pathak et al. (2019) observed that at higher O_2 concentration, as well as the higher RH and temperature, the greater the VUV photolysis efficacy to remove C_2H_4.

2.2.5 Catalytical oxidation processes

Catalytic oxidation is another method for C_2H_4 removal. This method involves the combination of C_2H_4 and O_2 (the oxidising agent) at elevated temperature in the presence of a catalyst such as oxides of copper, manganese and oxidization promoters (Pathak et al., 2017). The catalytic-based C_2H_4 oxidation reaction (Eq. 9) was described by Keller et al. (2013) as follows:

$$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$$

$$(\Delta G° = -1331\ kJ\ mol^{-1}) \quad (12)$$

A drawback of catalytic-based C_2H_4 scavenging systems is that they are mostly based on a platinum/alumina catalyst, operating at temperatures between 100 and 800 °C (Brecht, 2019). A modification of the catalytic oxidation system based on catalytic gas combustion was presented by Wojciechowski (1989). In such combustion technology, the C_2H_4-contaminated air was drawn by a fan and pumped into a platinum catalyst bed working at 180-250 °C. Later, an C_2H_4 catalytic combustion system based on Mn and Cu oxides and operating at 100-130 °C was reported by Blidi et al. (1993). Units based on catalytic oxidation can be considered an economically viable alternative to remove C_2H_4 from large storage facilities, showing a stable conversion efficiency of 90−98 % (Keller et al., 2013). Nevertheless, major disadvantages of these systems are that the catalysts are expensive, and the scavenger puts an extra heat load on the refrigeration system, resulting in dehumidification and additional energy requirement (Keller et al., 2013).

Catalytic systems using photocatalytic oxidation by UV light operating at temperatures below 100 °C (including at ambient or even sub-ambient temperatures) are also available (Brecht, 2019). Basically, this technique implies the exposition of a photon-elevated catalyst (usually metals such as Ag, ZnO, copper, palladium and TiO_2) to UV light (at approximately 380) to generate ROS, which further oxidise C_2H_4 (Gaikwad & Lee, 2017; Sadeghi et al., 2021). According to Pathak et al. (2017), when a semiconductor catalyst is UV irradiated with an energy greater than its band gap (the energy existing between the valence band and the conduction band), electrons in the valence band are displaced into the conduction band, leaving energy-rich electron-hole pairs in the band of origin (Pathak et al., 2017). For instance, Hu et al. (2019) suggested that nano-TiO_2 oxidises C_2H_4 as follows:

$$TiO_2 + h\nu \rightarrow TiO_2 + e^- + e^+ \quad (13)$$

$$H_2O + h^+ \rightarrow OH\cdot + H^+ \quad (14)$$

$$O_2 + e^- \rightarrow \cdot O_2^- \quad (15)$$

$$12OH \cdot + C_2H_4 \rightarrow 2CO_2 + 8H_2O \quad (16)$$

In the presence of O_2 and H_2O, the electron-hole pairs can produce hydroxyl ions (OH•), which then, disrupt C_2H_4 (Hu et al., 2019). Moreover, TiO_2 is usually supported onto an C_2H_4 adsorbing material such as saponite, MMT and fluorite to improve the C_2H_4 removal efficiency (Ooka et al., 2004). Besides the unneeded high temperature, the TiO_2-based photocatalytic systems do not require high pressure nor high energy demands, compared to thermal catalytic oxidation (Gaikwad & Lee, 2017). Nevertheless, the TiO_2 effectiveness in removing C_2H_4 can be affected by humidity, temperature, crystal size/phase and C_2H_4 and O_2 concentrations (Awalgaonkar et al., 2020).

2.2.6 Electron-deficient dienes or trienes-based ethylene scavengers

Other C_2H_4 scavengers that have been studied are those based on electron-deficient dienes or trienes, characterized by having withdrawing substituents (i.e. fluorinated alkyl groups, sulphones and esters) that react with C_2H_4 at room temperature (Gaikwad & Lee, 2017). The electron-deficient diene-or triene-based scavengers can be incorporated into films, bags and labels, or get into sachets for packaging applications. A disadvantage of these systems is that the moisture released from fresh produce must be overcome by using hydrophobic plastic films, since some electron-deficient dienes or trienes, such as triazine, are unstable under high moisture content (Gaikwad & Lee, 2017).

2.2.7 Plasma-catalytic oxidation

Trinh et al. (2015) reported the C_2H_4 removal by plasma-catalytic oxidation using Ag-based bimetallic catalysts (Ag-M_xO_y, where M corresponds to Co, Cu, Mn or Fe) supported on zeolite. In such a system, the C_2H_4 is adsorbed by a zeolite-supported Ag-M_xO_y, followed by the catalytic oxidation of the adsorbed C_2H_4 under plasma-activation conditions. The by-products of the C_2H_4 plasma-catalytic oxidation includes CO_2 mainly, and in lower concentrations CO, CH_4 and HCHO. Aerts et al. (2012) described the C_2H_4 decomposition by non-thermal plasma as follows:

$$C_2H_4 + N_2(A^3\Sigma_U^+) \rightarrow C_2H_3 + H + N_2 \quad (17)$$

$$C_2H_4 + O \rightarrow CH_2O + CH_2 \quad (18)$$

$$C_2H_3 + O \rightarrow CO + CH_3 \quad (19)$$

Trinh et al. (2015) found that O_3 was generated by plasma due to electrical discharges, which decreases as the temperature increases. Furthermore, the last authors observed that the C_2H_4 oxidation was strongly affected by the O_3 presence, but the O_3 can be degraded to metal oxides.

2.2.8 Biological filtration

Biological filtration is another technique that has been explored for C_2H_4 removal. In a biofilter, the C_2H_4-contaminated air flows through a packed material loaded with a film of C_2H_4-degrading microorganisms (Elsgaard, 2000; Kim, 2006; Kim, 2003). Then, C_2H_4 is immobilized into the biofilm and converted into CO_2, H_2O and organic biomass by microbial enzymatic oxidation and be further used as a carbon and/or energy source by microorganisms (Keller et al., 2013). The success of the biofiltration technology depends on the selection of appropriate C_2H_4-degrading microorganisms —which must have sufficient activity at low temperatures— and filter medium (Kim, 2006). This technology can be considered a cost-effective solution if it is operated at fairly low C_2H_4 concentrations, moderate temperature and high air flows (Elsgaard, 2000; Kim, 2003). A major disadvantage of biofilters is that at higher C_2H_4 airflow a larger biofilter is required and then, a larger installation spaced is needed (Keller et al., 2013). Moreover, biofiltration is a slow C_2H_4-degradation process and can have pressure drop issues (Pathak et al., 2017).

In conclusion, all of the hereby presented technologies are effective for removing C_2H_4, perhaps some more than others, but each tool has its pros and cons. Therefore, the right selection of an C_2H_4 scrubber will be determined by the desired application and factors like using in-packaging or storage rooms, long- or short-term transportation and the availability of resources. The sophisticated C_2H_4 removal technologies have a high effectivity, but they can be either tedious or uneconomical. For instance, a main drawback of the catalytical oxidation reaction is that it usually operates at high temperatures (< 100 °C), whereas the photochemical approach requires UV radiation to be activated. Regarding photocatalysis systems, they can operate at room temperature, but also need UV light. The requirement of UV light and/or high temperatures increase the running costs, besides implying a strong economic investment in equipment and operational costs, as well as in personnel training. Similarly, the C_2H_4 destruction by plasma may be expensive due to plasma reactor-related expenses (e.g. energy consumption). Moreover, such approaches are more appropriate for storage rooms rather than individual packages. Therefore, $KMnO_4$-based C_2H_4 tools are still very popular for the postharvest C_2H_4 control in fresh produce.

Finally, it should be remembered that, in order to increase profits, each of the C_2H_4 removal tools can be used in conjunction with another one, or with another type of technology such as controlled atmospheres, modified atmosphere packaging and inhibitors of C_2H_4 synthesis/action, among others (Martínez-Romero et al., 2007).

3 ADSORBENT MATERIALS USED IN POTASSIUM PERMANGANATE-BASED ETHYLENE SCAVENGERS

As mentioned in the previous section, chemical oxidation by $KMnO_4$ is the most used technology for scrubbing C_2H_4 in postharvest storage facilities (Sadeghi et al., 2021). $KMnO_4$ is an eco-friendly powerful oxidising agent in many organic and inorganic redox reactions that has gained importance in green chemistry (Dash et al., 2009). $KMnO_4$ oxidises C_2H_4 at ambient temperature to CO_2 and H_2O, passing through CH_3CHO and CH_3COOH, and releasing MnO_2 and KOH as by-products (Keller et al., 2013). However, $KMnO_4$ has a certain remaining degree of toxicity, and thus, it cannot be applied in direct contact with food products. To resolve this, $KMnO_4$ is immobilised on an inert solid support and it is packaged in filters or sachets that are placed inside the package, storage chambers or rooms, vehicles, and in domestic refrigerators (Martínez-Romero et al., 2007; Zagory, 1995). Thus, the C_2H_4-$KMnO_4$ interaction is governed by natural convection and diffusion, so it is required that the $KMnO_4$ support has a large contact area to facilitate the reaction (Keller et al., 2013; Varma, 1999; Wills & Warton, 2004).

The provision of an exposed large surface can be achieved with the help of nanotechnology. Supporting $KMnO_4$ onto inert solids of nanometric nature such as clays, zeolites, alumina, vermiculite and activated carbon can improve selectivity and reactivity of $KMnO_4$ (Álvarez-Hernández et al., 2018; Varma, 1999; Zagory, 1995). Furthermore, these materials can adsorb C_2H_4, resulting then, in an adsorption-oxidation system, where the support adsorbs C_2H_4 and the MnO_4^- ion oxidises it (Martínez-Romero et al., 2007). The effectiveness of a $KMnO_4$-based scrubber depends on many factors such as pore volume, pore size distribution and, especially, the support surface area, which should be large to facilitate the $KMnO_4$- C_2H_4 interaction (Zagory, 1995). Thus, the successful C_2H_4 scrubber design implies the appropriate selection of an inert support.

3.1 Metal oxides

3.1.1 Silica gel

Silica is a polymer of H_4SiO_4 with inter-linked SiO_4 arranged in a tetrahedral form, whereas silica gel is a granular form of silica with mesopores arranged in a hexagonal or cubic form (Jal et al., 2004). Silica gel surface chemistry is rich in -OH, or Si-O-H, which participate in adsorption as well as in chemical modifications (Yang, 2003). This material can be classified into two common types: low-density and regular density silica gels. The first one has a surface area of 300-350 $m^2\ g^{-1}$ and an average pore diameter of 100-150 Å, whereas the regular-density type has a surface area of 750-850 $m^2\ g^{-1}$ and a pore diameter 22-26 Å (Yang, 2003). Furthermore, silica gel is non-toxic and has excellent stability (both thermal and chemical), great accessibility, high specific surface area (up to 800 $m^2\ g^{-1}$) and great resistance to organic solvents (Jal et al., 2004; Polshettiwar et al., 2009). Spricigo et al. (2017) reported that 0.3 g silica nanoparticles with a surface area of 549.6 $m^2\ g^{-1}$ and an average pore size of 28.6 Å could reach a C_2H_4 adsorption rate of 34 ± 8 % after 1 h of exposure to 7.48 mL L^{-1} C_2H_4 at 25 °C and 90 % RH.

It is well known that silica gel is widely used as a desiccant due to its great capacity for H_2O absorption (Arvanitoyannis & Oikonomou, 2016), but its modified form with $KMnO_4$ has shown good results for C_2H_4 removal (Eastwell et al., 1978). Boller et al. (1983) used a column filled with $KMnO_4$ on silica gel to remove C_2H_4 produced by bean plants, reaching C_2H_4 levels below 2 nL mL^{-1}. Singh & Giri (2014) reported that $KMnO_4$ embedded on silica crystals was helpful to prolong the shelf-life of guava fruit (up to 7 weeks) reducing changes in firmness, SSC, TA and colour.

3.1.2 Activated alumina

Activated alumina is a semi-crystalline inorganic material composed mainly of Al_2O_3. It is prepared from aluminium salts by different methods, usually by thermal dehydration of $Al(OH)_3$ or gibbsite (Leyva-Ramos et al., 2008; Yang, 2003). The raw material used, and the preparation and activation methods determine the physicochemical and textural properties of activated alumina (Mallakpour & Khadema, 2015). Activated alumina has a surface area ranging from 50 to 500 $m^2\ g^{-1}$, a pore size ranging from 60 to 150 Å, and a pore volume of approximately 0.2-0.76 $cm^3\ g^{-1}$ (Leyva-Ramos et al., 2008; Srivastava & Eames, 1998). This porous material has both acidic and basic character with an acid site concentration of 0.35 meq g^{-1} and a basic site concentration of 0.58 meq g^{-1} (Leyva-Ramos et al., 2008).

Activated is often used as a desiccant similarly to silica, but it is also used for C_2H_4 adsorption (Tamon et al., 1981). Wills & Warton, (2004) reported an C_2H_4 removal of 90 % after 2.5-3 h when alumina beads containing 40 g kg^{-1} of $KMnO_4$ were evaluated at 20 °C and 60-70 % RH. Spricigo et al. (2017) reported that 0.3 g alumina nanoparticles (93.59 m^2 g^{-1} surface area and 20.6 Å average pore size) reached an ERR of 21 % after 1 h when they were exposed to 7.48 mL L^{-1} C_2H_4 at 25 °C and 75 % RH, but when these nanoparticles were impregnated with 5 and 10 % $KMnO_4$, they showed an ERR of 82 and 100 %, respectively.

Activated alumina beads impregnated with $KMnO_4$ are mainly used as C_2H_4 scavenger for extending the shelf life of fresh fruit and vegetables (Jayraman et al., 1992; Lidster et al., 1985). Although there are not many reports on the use of $KMnO_4$ impregnated on activated alumina beads, a lot of commercial products are available such as Purafil (Purafil, Doraville Ga.), Circul-Air (Circul-Aire, Montreal), Ethysorb (Molecular Products and Air Repair® (DeltaTrak, Inc.). Wills & Kim (1995) studied the effect of 10 g of activated alumina impregnated with $KMnO_4$ on 250 g of strawberry, reporting a reduction of C_2H_4 and CO_2 levels. However, some authors reported that this kind of scavengers has limited efficacy in environments with high RH (Terry et al., 2007; Wills & Warton, 2004).

3.2 Layered silicates and zeolites

3.2.1 Vermiculite

Vermiculite is a 2:1 layered silicate composed of two tetrahedral sheets with a $[T_4O_{10}]^{4-}$ composition (where T can be Si^{4+}, Al^{3+} or Fe^{3+}) and an octahedral sheet formed by two planes of packed O^{2-} and octahedral OH^- anions with Mg^{2+} or Al^{3+} as central cations (Valášková & Martynkova, 2012). It results from the alteration of biotite and iron-bearing phlogopite, chlorite, pyroxene, or other similar minerals by weathering, hydrothermal action or percolating groundwater (Marcos et al., 2009). The interlayer space of vermiculite is between 0.149 and 0.153 nm, and the thickness of the structural unit (2:1 layer and interlayer space) is approximately 1.4 nm, depending on the interlayer cations and interlamellar H_2O content (Valášková & Martynkova, 2012). The specific surface area is from 1.4 to 720 m^2 g^{-1} (Maqueda et al., 2007; Temuujin et al., 2003). The highest specific surface area values are achieved when the material is subjected to treatment (either acid, mechanical or both). This phyllosilicate has a negative layer charge resulting from the substitution of Si^{4+} by trivalent cations in tetrahedral positions or from site vacancies at the sheets, but this charge is neutralised by the presence of hydrated cations in the interlayer

space (Reinholdt et al., 2013). It has a cation exchange capacity of 120-150 meq 100 g^{-1} (Malandrino et al., 2006).

Vermiculite impregnated with $KMnO_4$ has been widely used as C_2H_4 scavengers to prolong the shelf-life of fresh produce. However, there are not good results. For example, avocado stored in polyethylene bags with vermiculite-$KMnO_4$ C_2H_4 scavenger for 10 days showed a higher concentration of C_2H_4 than those samples without the scavenger (Chaplin & Hawson, 1981). Di Tonno et al. (1991) also found that $KMnO_4$ impregnated vermiculite was not effective for C_2H_4 removal on kiwifruits storage. In another study, sets of papaya were wrapped in polyethylene films with vermiculite-based C_2H_4 scavenging sachets for 25 days (Pereira et al., 2009). After this period, CO_2 concentration, fresh matter loss, and SSC increase were lower in the bags with scavenger than those without it, whereas peel colour index, pulp consistency, and electrolyte leakage did not show a statistical difference between means.

3.2.2 Clays

Clays are hydrous layer silicates of colloidal dimensions (around 1 nm-150 µm), with tetrahedral and octahedral layers (Bhattacharyya & Gupta, 2008; Rouquerol et al., 1999; Varma, 2002). The centre of the tetrahedral layers consists of sheets of Si^{4+}, but Al^{3+} is also common, whereas the octahedral layers consist of generally Mg^{2+} or Al^{3+}, but Fe^{2+}, Ni^{2+}, Li^{+}, Fe^{3+}, Cr^{3+} may also be present. Depending on the degree of occupancy of the octahedral sites, the octahedral layers are classified into trioctahedral and dioctahedral, having a different arrangement of layers. Clays arranged by alternating tetrahedral and octahedral sheets are clays with 1:1 structure (e.g. kaolinites), whereas those formed by an octahedral sheet placed between two tetrahedral sheets are 2:1 kind (e.g. smectite), and clays consisting of alternating three 2:1-kind units and one brucite layer are 2:1:1 structure (e.g. chlorite) (Varma, 2002). Because of the layer configuration, this group is called phyllosilicate (Rouquerol et al., 1999).

Clays are characterised by high surface area, swelling, and intercalation and cation-exchange with other ions without affecting the structure (Bhattacharyya & Gupta, 2008). Moreover, they are eco-friendly, non-toxic, economical and recyclable. Therefore, it is useful to be modified through ion exchange procedures with other positive charged atoms or organic ions (Avalos et al., 2008). Smectite group, as mentioned above, is a kind 2:1 clay mineral with an interlayer spacing around 10 and 15 Å, where MMT is the most common member of this kind of clay (Varma, 2002). MMT has an interlayer spacing of approximately 0.9 to 1.2 nm and great cation exchange capacity (Kaur & Kishore, 2012). MMT has been

used as $KMnO_4$, but its applications are focused mainly on adsorption of heavy metals (Abollino et al., 2003; Bhattacharyya & Gupta, 2008), oxidation of alcohols and alkylarenes, among other organic compounds (Noureldin & Lee, 1981; Ahmad Shaabani et al., 2002, 2004). There is only one report on its implementation for the oxidation of alkenes (Choudary et al., 1991) and we did not find a report which explicitly mentions the application of $KMnO_4$ supported on MMT to extend the postharvest life of fresh produce.

Nevertheless, some studies report the use of clays, although the clay type is not clarified. For example, Chamara et al. (2000) packaged banana fruit under MAP with $KMnO_4$ supported on clay bricks at 25 °C, reporting an extended green life up to 20 days, in contrast to 4 days for untreated fruit. Compared with fruit stored without the C_2H_4 scrubber, little changes in firmness and SSC, lower C_2H_4 and CO_2 contents, and higher O_2 levels were found. Santosa et al. (2010) also applied a $KMnO_4$-based C_2H_4 scrubber using clay as the support to prolong the shelf life of banana fruit. They noted that a dose of 30 g of scrubber per kg of fruit was enough to delay the peel yellowing, to reduce weight and hardness losses, and to minimise the SSC increase and acid content up to 18 days.

3.2.3 Zeolite

Zeolites are volcanic aluminosilicates crystalline materials of alkali or alkali earth elements (Alver, 2013). Zeolites show a three-dimensional framework with a first complexity characterised by a chemical disorder in frameworks of SiO_4 and AlO_4 tetrahedral molecules that are assembled to form secondary polyhedral building units (e.g. cubes, hexagonal prisms and octahedral, etc.), and with interconnected cages and channels, known as pores (Coombs et al., 1997; Patdhanagul et al., 2012; Yang, 2003). These materials can be natural or synthetic with more than one hundred characterised crystalline structures (Martínez-Romero et al., 2007; Millar et al., 2016). There are over 40 natural zeolites (e.g. chabazite, gmelinite, and mordenite) and more than 150 types of synthetic zeolites (e.g. types A, X, Y, ZSM, etc.) (Yang, 2003). Until 2004, it was considered that zeolite Y had the highest surface area (904 $m^2\ g^{-1}$), but with the introduction of zeolite-type metal-organic framework materials, this was exceeded, with values up to 3,000 $m^2\ g^{-1}$ (Chae et al., 2004; Jiang et al., 2011). Usually, channels and cages have six-membered rings with a manipulable size ranging from 3 to 10 Å. The size can be modified by fixing the type and number of cations allowing a better selectivity of sorption (Coombs et al., 1997; Yang, 2013).

Zeolites have a high adsorbent capacity and selectivity; they are capable of separate specific molecules from gas mixtures according to their selective pore dimension and configuration or polarity (Piergiovanni et al., 1992). Therefore, zeolites can act as a

molecular sieve and also as an ionic exchanger (with a cation exchange capacity of 2-2.7 meq 100 g^{-1}) (Burcu Erdoğan et al., 2008; Limtrakul et al., 2001; Patdhanagul et al., 2012). Due to these properties; these materials have been commonly used to remove C_2H_4. Monprasit et al. (2011) found that hydrophobic zeolite shows high C_2H_4 adsorption selectivity, and Aday & Caner (2011) reported that sachets containing 2 g of chabazite zeolite could adsorb C_2H_4 at a rate of 1.35 mL g^{-1}. In another study, Peiser & Suslow (1998) reported an adsorption of 3.3 µL g^{-1} by heat-treated chabazite zeolite, while clinoptilolite zeolite did not show C_2H_4 adsorption capacity.

In addition, there are several studies about the application of $KMnO_4$ absorbed onto zeolite to remove C_2H_4 during storage of fruit and vegetables. For example, Salamanca et al. (2014) studied the effect of three doses of a zeolite and $KMnO_4$ mix on tomato 'Chonto' fruit. The treatment consisting of zeolite 1.5 % and $KMnO_4$ 1.5 % (based on fresh weight) showed the best performance by presenting the lowest weight loss and SSC, and high strength and, thus delaying the ripening process. In another study, 'Golden Delicious' apples were stored with $KMnO_4$-coated nano-zeolite sachets, for five months at 0 °C and 90 % RH. They showed a lower pH increase, lower TA percentage decrease, lower firmness loss and lower change in H_{ab} angle than untreated apples, which indicates that the ripening process was delayed (Sardabi et al., 2014).

$KMnO_4$-coated zeolites filter mode is also available. Rezai et al. (2008) reported that applying $KMnO_4$ and zeolite-based nano-molecular filters resulted in lower weight loss, higher texture firmness and longer shelf life (over 20 days of storage) of Iceberg lettuce and Chinese cabbage. Similar results were found when this filter system was evaluated on apricot (Emadpour, Kalaj, et al., 2009), peach and nectarine (Emadpour et al., 2015). The ability to remove C_2H_4 by $KMnO_4$ supported on zeolite was studied by Peiser & Suslow, (1998), who found an C_2H_4 removal capacity of around 929 µL g^{-1} h^{-1}.

3.3 Activated carbon

Activated carbon is a non-crystalline material with a porous structure. It is characterised by showing heterogeneous surfaces, which is attributed to their different heteroatoms that assume the character of functional groups (mainly O_2) as well as their differences in sizes and shape of pores, and cracks and pits (László et al., 2003). The surface chemistry (heteroatomic functional groups) are in function of the nature of the raw material (Dąbrowski et al., 2005). The raw material is often of lignocellulosic origins such as wood, coals, petroleum coke, bones, coconut shell, fruit nuts or any other carbonaceous material (Puziy et al., 2002), but the selected one should have low inorganic matter content, be easily

activated, easy availability with low cost, and low degradation rate upon storing (Reinoso, 1997). The activation step is carried out to create more pores and changes the pore volume, form and size (Dąbrowski et al., 2005). For food-grade, activated carbons have pore volumes between 10 to 25 Å in diameter and surface area ranging from 237 to 2000 m^2 g^{-1}, but some of them can reach surface areas up to 5000 m^2 g^{-1} (Martínez-Romero et al., 2007; Yang, 2013).

Activated carbons can be granular, powdered or fibre, being the granular form the most preferred due to its easier regeneration and versatility (Carrott et al., 2001). In addition, there has been reported that the best C_2H_4 adsorption is performed by the granular form (over 80 %) in comparison with the powder and fibre forms (Martínez-Romero et al., 2007). Bailén et al. (2006) found that granular-activated carbon (226 m^2 g^{-1} specific area) can maintain significantly lower C_2H_4 levels in packages of tomato fruit up to two weeks in comparison with packages without activated carbon.

Activated carbon is often combined or impregnated with other compounds such as $KMnO_4$ to increase effectiveness. However, while it is mentioned in several reviews that activated carbon and $KMnO_4$ have been used together as C_2H_4 scavengers (Brody et al., 2008; Gavara et al., 2009; Sen et al., 2012), there is a dearth of literature about its application and on the amount of C_2H_4 that this kind of tool can remove. Air cleaning filter is an invention based on activated carbon fibres supporting $KMnO_4$ (Ishii et al., 1998). According to inventors, it is important to clarify that $KMnO_4$ and activated carbon combination will result in active MnO_2 (an insoluble and powerful oxidising agent) due to a redox reaction.

4 CURRENT SCENARIO OF POTASSIUM PERMANGANATE-BASED ETHYLENE SCAVENGERS IN POSTHARVEST TECHNOLOGY

$KMnO_4$-based C_2H_4 scavenging technology has been widely used for almost 50 years. The first report on the $KMnO_4$ application in C_2H_4 scavenging systems for fresh fruit preservation dates from 1967 (Forsyth et al., 1967). Early studies were on the storage of apples and bananas, where Forsyth et al. (1967) and Scott et al. (970), respectively, found that $KMnO_4$ can be useful to delay the ripening process. Since then, large research on the responses of both climacteric fruit and non-climacteric produce has been developed (Álvarez-Hernández et al., 2019). Most research has been largely centred on climacteric fruit, particularly in apple and banana cultivars. Moreover, $KMnO_4$–based C_2H_4 scavenging products can be also used to protect floral products from C_2H_4 detrimental damage (e.g., flower abscission or wilting, epinasty of buds and flowers and leaf shedding), maintaining their good appearance and extending their shelf life (Araújo et al., 2013; Ketsa et al., 2003).

Nowadays, several $KMnO_4$–based products engineered for C_2H_4 scavenging applications are commercially available. As presented in Table 2, commercial C_2H_4-scavengers have been developed in different shapes (beads, cylindrical and irregular pellets and powder) containing 3.5-12 % *w/w* $KMnO_4$.

According to the available information, currently available products in the market have an C_2H_4 scavenging capacity ranging from 3 to 6.5 L kg^{-1}. Furthermore, there are some commercial $KMnO_4$-based products such as Bi-On® SORB (Bioconservacion S.A., Barcelona, Spain), Chemisorbant (Purafil, Inc., Doraville GA, USA), MM-1000 MULTI-MIX® MEDIA (Circul-Aire Inc., Montreal, Canada) and Sofnofil™ (Molecular Products Limited, Essex, UK), which are not specifically intended for the removal of C_2H_4 but are marketed as broad-spectrum contamination control materials for air purification in industrial applications.

Table 2. $KMnO_4$–based ethylene scavengers currently available in the market (source: Own elaboration).

Trade name (manufacturer)	General description	C_2H_4 scavenging capacity (L kg^{-1})	General characteristics	Commercially available presentations	Application guidelines	Reference
Air Repair™ (DeltaTrack Inc., Pleasanton CA, USA)	Activated aluminum impregnated with $KMnO_4$	NS	Shape: Spherical pellets	Bulk beads/ Sachet/ Tube/ Blanket	NS	DeltaTrack Inc. (2018)
BEfresh (Befresh Technology, S.L., Barcelona, Spain)	Natural clays impregnated with $KMnO_4$	4.5	Shape: Cylindrical pellets	Sachet/ Tube/ Module	NS	Befresh Technology (2018b, 2018a)
BEfresh+ (Befresh Technology, S.L., Barcelona, Spain)	Natural clays impregnated with $KMnO_4$	6.5	Shape: Cylindrical pellets	Sachet/ Tube/ Module	NS	Befresh Technology (2018b, 2018a)
Bi-On® R8 (Bioconservacion S.A., Barcelona, Spain)	Natural clays impregnated with 8 % $KMnO_4$	3.5	Shape: Cylindrical pellets Bulk density: 0.84 g mL^{-1} Pellet diameter: 2.3-4 mm Moisture content: 15-20 %	Bulk granules/ Sachet/ Tube/ Machine/ Module	Temp.: -20-50 °C RH: 10-95 %	Bioconservacion (2015)
Bi-On® R12 (Bioconservacion S.A.,Barcelona, Spain)	Natural clays impregnated with 12 % $KMnO_4$	4.5	Shape: Cylindrical pellets Bulk density: 0.84 g mL^{-1} Pellet diameter: 2.3-4 mm Moisture content: 15-20 %	Bulk granules/ Sachet/ Tube/ Machine/ Module	Temp.: -20-50 °C RH: 10-95 %	Bioconservacion (2015a)

Table 2. Continued.

Trade name (manufacturer)	General description	C_2H_4 scavenging capacity (L kg^{-1})	General characteristics	Commercially available presentations	Application guidelines	Reference
BIOPAC (Biopac Pty Ltd, West Burleigh, Australia)	Porous material mixed with $KMnO_4$	2.8-4.2	Shape: Spherical pellets	Tube/ Sachet/ Module	NS	Biopac (n.d.)
BioX® 4.0 (BioXTEND Co., Fort Myers FL, USA)	Alumina mixed with 4.0-4.5 % $KMnO_4$	2.8-3.0	Shape: Spherical pellets Pellet diameter: 3.0 mm Moisture content: 15-20 %	Bulk granules/ Tube/ Sachet/ Module	NS	BIOXTEND (2012)
BioX® 8.0 (BioXTEND Co., Fort Myers FL, USA)	Alumina mixed with 8.0-8.5 % $KMnO_4$	3.4	Shape: Spherical pellets Pellet diameter: 3.0 mm Moisture content: 15-20 %	Bulk granules/ Tube/ Sachet/ Module	NS	BIOXTEND (2012)
BRYSORB™ 508 (Bry-Air (Asia) Pvt Ltd, Gurugram, India)	Activated alumina impregnated with $KMnO_4$	NS	Shape: Spherical beads Pellet diameter: 2.5-3.5 mm Bulk density: 0.85-0.90 g mL^{-1} Moisture content: 20-25 %	Bulk granules	Temp.: -20-50 °C RH: 10-95 %	Bry-Air (Asia) Pvt. Ltd. (2017)

Table 2. Continued.

Trade name (manufacturer)	General description	C_2H_4 scavenging capacity (L kg^{-1})	General characteristics	Commercially available presentations	Application guidelines	Reference
Eris filter (Miatech, Inc., Clackamas OR, USA)	$KMnO_4$ pellets	NS	Shape: Spherical pellets	Blanket	NS	Miatech Inc. (2019)
Ethysorb ® (Molecular Products Limited, Essex, UK)	Activated alumina impregnated with 3.5-5 % $KMnO_4$	NS	Shape: Spherical pellets Bulk density: 1 g mL^{-1} Particle size: 2.5-5.0 mm Relative density: 3.3 g mL^{-1}	Bulk beads/ Tube/ Blanket	Temp.: -10-40 °C RH: 10-95 %	Molecular Products Limited (2009)
Extend-A-Life™ (AgraCo Technologies International, LLC, Dillsburg PA, USA)	Zeolite coated with 8 % $KMnO_4$	NS	NS	Sachet/ Filter	NS	AgraCo Technologies International LLC (n.d., 2014)
GK3 (Greenkeeper Iberia, S.L., Madrid, Spain)	Phyllosilicate and aluminosilicate loaded with 8 % $KMnO_4$	3.4	Shape: Cylindrical pellets Particle diameter: 2.0, 3.0 and 4.0 mm Moisture content: 15 %	Tube/ Machine/ Module	NS	Flink (n.d.); GreenKeeper (ND); GreenKeeper Iberia SL (n.d.)

Table 2. Continued.

Trade name (manufacturer)	General description	C_2H_4 scavenging capacity (L kg^{-1})	General characteristics	Commercially available presentations	Application guidelines	Reference
GK4 (Greenkeeper Iberia, S.L., Madrid, Spain)	Phyllosilicate and aluminosilicate loaded with 12 % $KMnO_4$	4.2	Shape: Cylindrical pellets Particle diameter: 2.0, 3.0 and 4.0 mm Moisture content: 15 %	Tube/ Machine/ Module	NS	Flink (n.d.); GreenKeeper (n.d.); GreenKeeper Iberia SL (n.d.)
Retarder® (Retarder SRL, Verzuolo, Italy)	Mix of clays and oxidizing agents (such as $KMnO_4$)	NS	Shape: Cylindrical pellets	Sachet/ Tube	NS	Retarder SRL (n.d.)
Ryan® (Sensitech Inc., Beverly MA, USA)	Mixture of natural clays and 6 % $KMnO_4$	3.0	Shape: Cylindrical pellets Pellet diameter: 3.0 mm	Sachet/ Tube	NS	Sensitech Inc. (2013)
Select (Purafil, Inc., Doraville GA, USA)	Activated alumina impregnated with 8 % $KMnO_4$	NS	Shape: Spherical pellets Bulk density: 0.8 g mL^{-1} Pellet diameter: 3.2 mm Moisture content: ≤ 35 %	NS	Temp.: -20-51 °C RH: 10-95 %	Purafil, Inc. (2015, 2019)
Keepcool (Keepcool, Molina de Segura, Spain)	Sepiolite mixed with $KMnO_4$ and activated carbon	NS	Shape: Irregular granules Particle size: 0.6-0.3 mm	Sachet/ Filter/ Machine	NS	Keepcool (2018a, 2018b); Climent (2015)

Table 2. Continued.

Trade name (manufacturer)	General description	C_2H_4 scavenging capacity (L kg^{-1})	General characteristics	Commercially available presentations	Application guidelines	Reference
Keepfresh (Blue teck systems, S.L., Madrid, Spain)	Natural zeolite impregnated with 6 % $KMnO_4$	NS	NS	Sachet/ Sheets/Tube/ Machine	NS	Keepfresh (2018); Köstekli et al. (2016)
Super Fresh Media (Ethylene Control, Inc., Selma CA, USA)	Natural zeolite impregnated with 4-6 % $KMnO_4$	NS	Shape: Irregular granules	Bulk beads/ Sachet/ Blanket		Ethylene Control Inc. (2015)

RH: Relative humidity; NS: Not specified; n.d.: No date.

4.1 Ethylene removal reaction and application form of the potassium permanganate-based ethylene scavengers

The active agent $KMnO_4$ is usually supported on a porous C_2H_4 adsorber substrate with a large surface area, typically alumina (Table 2), to facilitate the redox reaction (Kader, 2002; Shaabani et al., 2007). As the reaction proceeds, a gradual colour change from purple to dark brown occurs because the MnO_4^- ion is reduced into MnO_2 (Martínez-Romero et al., 2007; Wills & Warton, 2004). This phenomenon can be observed in Figure 6 and 7. These figures show the C_2H_4 breakthrough measurement on a $KMnO_4$-based C_2H_4 scavenger (Bi-On® R12, Bioconservacion S.A., Barcelona, Spain) held under a continuous C_2H_4-enriched airflow (5,000 ppm at 120 mL min^{-1}) at room temperature (22 ºC), and the changes in $KMnO_4$ concentration (%) and colour that occur in the material over time.

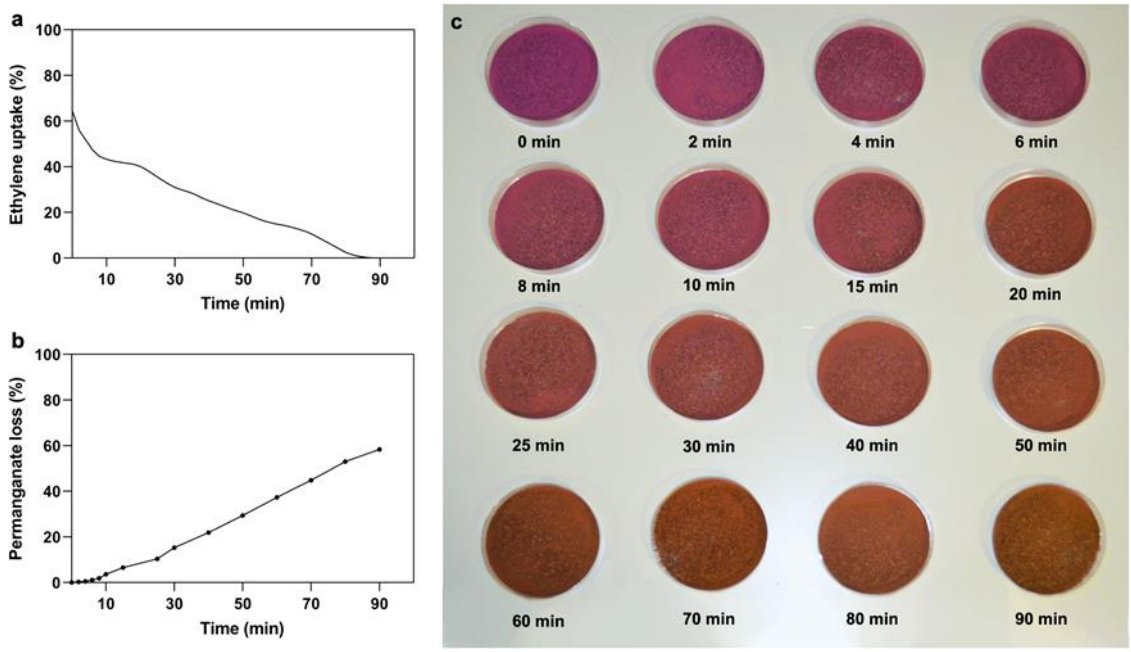


Figure 6. Changes in C_2H_4 uptake capacity of a $KMnO_4$-based C_2H_4 scavenger (Bi-On® R12, Bioconservacion S.A.) (a) *vs* $KMnO_4$ concentration (b) and visual colour change image (c) material over time (source: Own elaboration).

$KMnO_4$-based C_2H_4 scavengers are mainly used in sachet form for food packaging application but can also be found in different presentation forms such as blankets or filter tubes that can be placed in warehouses or transport chambers; incorporated into household refrigerators systems, or directly incorporated into the packaging material (de Abreu et al., 2017; Janjarasskul & Suppakul, 2018; Martínez-Romero et al., 2007). For instance, Taboada-Rodríguez et al. (2013) reported that barrier properties of the cardboard material usually used in food packaging could be improved by applying a coating made of polylactic acid and $KMnO_4$ supported onto SP. However, $KMnO_4$ is not typically integrated into food

contact surfaces of food packaging because of its toxicity and colour (Bodbodak & Rafiee, 2016; Gaikwad & Lee, 2017).

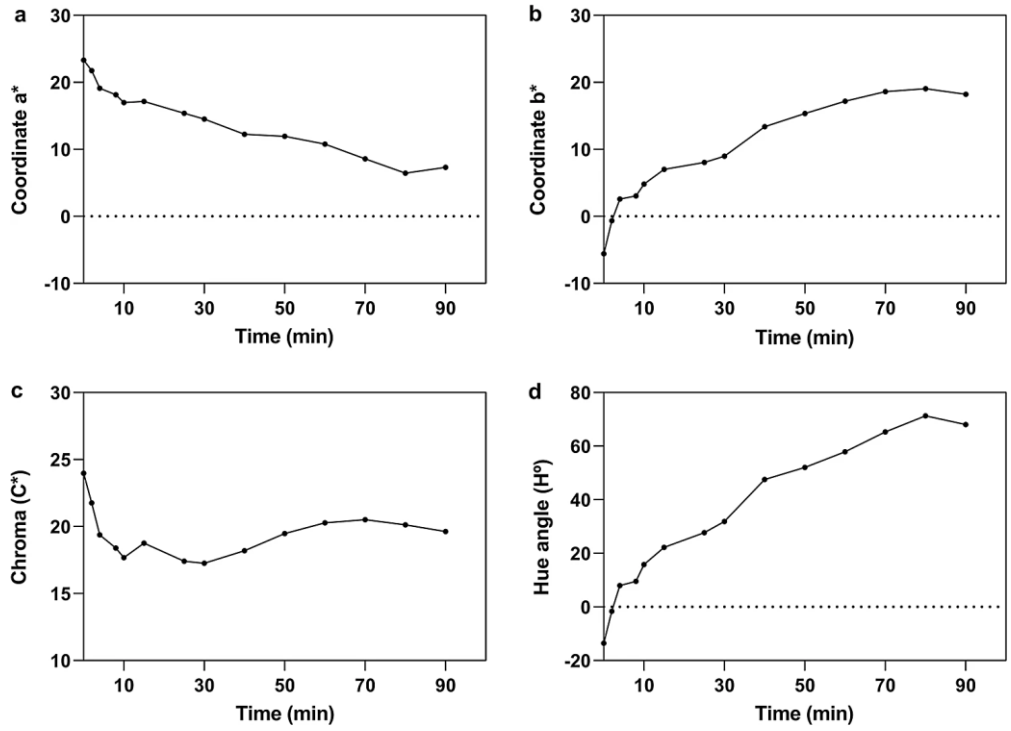


Figure 7. Evolution of colour parameters *a*, b*,* C* and H_{ab} overtime for a $KMnO_4$-based C_2H_4 scavenger (Bi-On® R12, Bioconservacion S.A.) held under a continuous C_2H_4-enriched airflow (source: Own elaboration).

In a commonly individual C_2H_4 scavenging packaging system (Figure 8), a sachet containing the C_2H_4 scavenger product is placed within the produce package (Janjarasskul & Suppakul, 2018), at the upper part of the package (Mortazavi et al., 2015; Sharma & Ghoshal, 2018). At this point, it should be clarified that the most suitable position to attach a scavenger- or a release- sachet will depend on the density of the gaseous compound to be scrubbed or released, respectively. The density of a gas can be deduced from the Ideal Gas Law (Eqs. 20-23):

$$P \times V = n \times R \times T \tag{20}$$

$$P \times V = \frac{m}{V} \times R \times T \tag{21}$$

$$\frac{P \times V}{R \times T} = \frac{m}{M} \tag{22}$$

$$d = \frac{P \times M}{R \times T} \tag{23}$$

where *P* is the atmosphere (atm), *M* is the gas molar mass (g mol^{-1}), *R* is the gas constant (0.082 atm L $(K\ mol)^{-1}$) and *T* is the temperature (K).

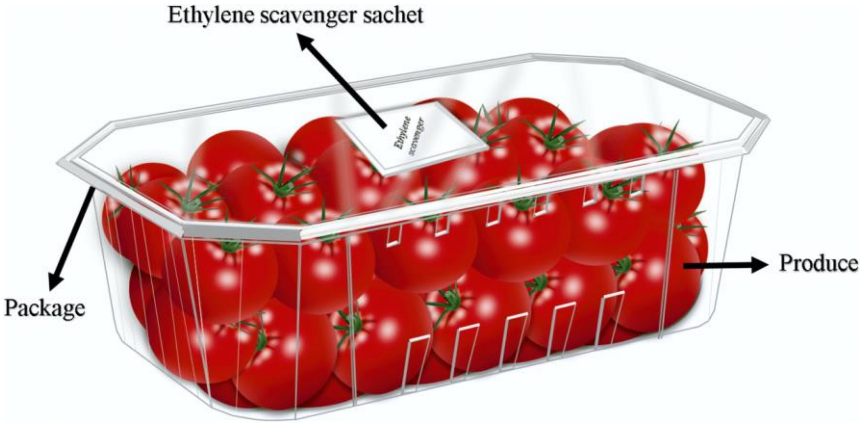


Figure 8. Schematic representation of an C_2H_4-scavenger sachet used in horticultural produce packaging (source: Own elaboration).

Therefore, since C_2H_4 tends to rise to the top of the package because it is slightly less dense than air (for instance, the C_2H_4 and air densities are 1.16 and 1.20 g mol^{-1}, respectively, at 22 ºC and 1 atm), the upper part of the package seems to be the most suitable position to attach an C_2H_4 scavenger sachet. Then, the sachet material must be highly permeable to the C_2H_4 gas molecule, allowing C_2H_4 uptake from the in-package atmosphere through a convection and diffusion mechanism (de Kruijf et al., 2002; Yildirim et al., 2018). Some typically used sachet materials reported in the literature are PE, muslin cloth or cellulose (El-Anany & Hassan, 2013; Mujtaba et al., 2014). In general, the commercially available active packaging agents such as $KMnO_4$–based products are typically packed into heat-sealed Tyvek® film sachets (Wyrwa & Barska, 2017). DuPont™ Tyvek is a HDPE film (Figure 9) that meets the USA and EU regulations for food contact applications (DuPont, 2018).

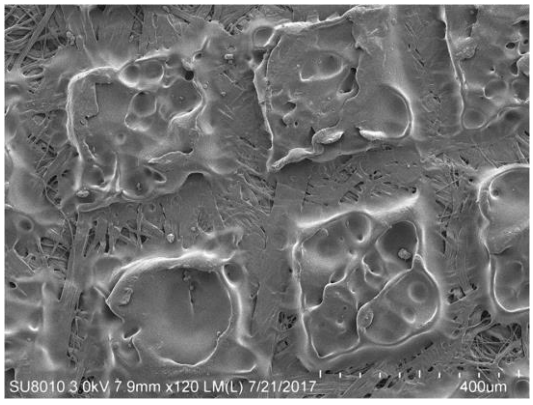


Figure 9. Scanning electron microscope image of DuPont™ Tyvek® material used for $KMnO_4$ sachets (source: Own elaboration).

4.2 Human health and environmental concerns

Although there are already several registered commercial $KMnO_4$–based products (Table 2), the active packaging use in the European market is just beginning to increase (Vilela et al., 2018). Gaikwad & Lee (2017) and Vilela et al. (2018) attributed such behaviour to low consumer acceptance and strict legislation. Even though $KMnO_4$–based C_2H_4 scavengers are commonly placed into individual sachets to keep products free from contamination, and to avoid human health risks associated with $KMnO_4$ poisoning, there is still concern about possible $KMnO_4$ migration. In this sense, it is highly recommended to avoid direct exposure to $KMnO_4$, particularly, at concentrated solutions and to undiluted $KMnO_4$ (CDC, 2015).

Furthermore, $KMnO_4$ can be harmful if it is swallowed, being classified as H302 by the GHS of Classification and Labelling of Chemicals (UNECE, 2009). Therefore, it is true that $KMnO_4$-based products must be carefully handled. Nonetheless, it is well documented that the risk of $KMnO_4$ intoxication is not common, being approximately 142.9 mg kg^{-1} (10 g of $KMnO_4$ per a person weighing 70 kg) the lethal adult dose and 750 mg kg^{-1} the oral LD50 rat dose (Cevik et al., 2012; WHO, 1981). In addition, $KMnO_4$ is not listed on the WHO Acute Hazard Rankings (WHO, 2010). Furthermore, $KMnO_4$ is commonly used at low concentrations in highly-diluted solutions as an antiseptic and antifungal drug and it is included in the WHO Essential Medicines List (WHO, 2017). $KMnO_4$ as an indirect food additive is regulated by the FDA under the Code of Federal Regulations (CFR; 21 CFR §175.105 2018). General USA FDA requirements for food contact applications are also established through the CFR (21 CFR §177.2210 2018 and 21 CFR §177.1520 2018), while the EU has specific requirements related to active packaging and its non-active parts that are regulated by the Regulation 1935/2004/EC and Regulation 450/2009/EC (EC, 2004; EC, 2009). Particularly, Regulation 450/2009/EC establishes a legal basis for active packaging safety and marketing (Janjarasskul & Suppakul, 2018). The regulation aspects of the EU and USA concerning active and intelligent food packaging have been extensively discussed by Dainelli et al. (2008) and Restuccia et al. (2010).

On the other hand, the high oxidizing power, either in heterogeneous conditions or without solvents, makes $KMnO_4$ and its compounds of particular environmental concern. However, the $KMnO_4$ oxidation process is considered to be eco-friendly (Dash et al., 2009). In fact, $KMnO_4$ has been defined as a green oxidant in organic chemistry since the inorganic coproducts (particularly, MnO_2) can be re-oxidized to permanganate, providing a sustainable approach (Shaabani et al., 2007; Singh & Lee, 2001). Therefore, as a green oxidant, $KMnO_4$ has been widely used in industrial and agricultural processes, including air

purification (by removing C_2H_4, pollutants such as SO_2, H_2S, aldehydes and other volatile organic compounds); H_2O treatment to remove pollutants such as algal toxins and pharmaceuticals; as a bleaching agent in the textile industry; and as an antimicrobial agent in pesticide products (Dash et al., 2009; Singh & Lee, 2001; Tirgar et al., 2018).

$KMnO_4$ is not listed in the WHO Environmental Health Criteria Documents (WHO, 2018). However, since $KMnO_4$ is typically used at full-scale for H_2O treatment applications (EPA, n.d; Guan et al., 2010), it is regulated by the United States EPA under the chemical code number 068501 because high doses can be harmful to aquatic life (EPA, 2018). $KMnO_4$ is classified by the GHS as a very toxic agent to aquatic organisms under the code number H400 and H410 (UNECE, 2009). Hence, $KMnO_4$-based products should not be released into the environment (prevent from reaching H_2O bodies such as lakes and rivers, soil and sewage systems). In addition, since $KMnO_4$ is a strong oxidant agent, it can enhance the combustion of other substances and can also release irritating or toxic fumes in a fire, thus $KMnO_4$-based products should be stored and disposal separated from reducing, flammable and combustible substances (CDC, 2015). Nevertheless, in $KMnO_4$-based C_2H_4 scavengers, $KMnO_4$ is commonly supported onto a solid material such as alumina, zeolite or silica, which interfere with the aforementioned MnO_2 re-oxidation process (Shaabani et al., 2007). The latter leads to non-toxic and chemically inert by-products that do not represent an environmental concern and can be disposed of as normal waste (Keller et al., 2013; Santos & Rosas, 2016).

Therefore, $KMnO_4$-based C_2H_4 scavengers can be considered as an environmental–friendly tool that can be used in active packaging technology for horticultural products, with the proper handling and the relevant safety measures.

4.3 Effects of potassium permanganate-based ethylene scavengers on postharvest quality of fresh produce

As earlier mentioned, large research on the $KMnO_4$ effects on the quality attributes of both climacteric fruit and non-climacteric produce has been developed. Most of the studies concerning the effects of $KMnO_4$ on fresh horticultural products have been carried out on climacteric fruit, mainly on apple and banana, which are high producers of C_2H_4 and are very sensitive to it (Blanke, 2014).

However, cultivar, maturity stage, storage period and storage conditions, as well as the presence of exogenous C_2H_4 during storage or transportation are some factors that may

counteract the effect of these $KMnO_4$-based tools (Palou & Crisosto, 2003). For instance, in climacteric fruit, the rate and intensity of C_2H_4 production are higher at the ripe stage, regarding mature and half-ripe stages (Blanke, 2014). The latter fact can be observed in the studies carried out by Bhutia et al. (2011) and do Amarante & Steffens (2009b, 2009a), who evaluated the effect of $KMnO_4$–based C_2H_4 scavengers on 'Kallipati' sapote, 'Gala' apple and 'Royal Gala' apple at different ripening stages. The results indicated that the C_2H_4 scavengers may retard the physiological and physicochemical processes in sapote and 'Gala' apple independently of the maturity stage, although the effects were more pronounced in fruit harvested and stored at a mature stage (Bhutia et al., 2011; do Amarante & Steffens, 2009a). Meanwhile, the influence of the maturity stage on the efficiency of C_2H_4 scavengers was found to be more marked in 'Royal Gala' apple (do Amarante & Steffens, 2009b). do Amarante & Steffens (2009b) reported that, despite having removed the total amount of C_2H_4 inside the apple package at each maturation stage, it was only possible to delay the ripening process in fruit harvested at less advanced maturation stage, while in fruit with a higher maturity stage no significant effect was observed. The last authors attributed such results to the fact that the C_2H_4 production rate increases along with the ripening process, causing a higher accumulation of C_2H_4 inside the package and hindering the C_2H_4 removal efficiency. Thus, the effect of C_2H_4 scavengers to delay the ripening process and to extend the fruit and vegetable shelf life is more evident when they are harvested at the mature green stage. Therefore, it is recommended to harvest fruit and vegetables at the latter maturation stage or before the autocatalytic production of C_2H_4 in order to obtain the maximum benefit from the C_2H_4 scavengers.

In addition, due to the responses to $KMnO_4$-based C_2H_4 scavengers may vary between cultivars, in the following subsections, apple, banana, mango and tomato are used to illustrate the range of responses to $KMnO_4$-based C_2H_4 scavengers since most of the literature available focuses on the study of such products. Nonetheless, an outline of general responses of other climacteric fruit and non-climacteric produce to $KMnO_4$-based C_2H_4 scavengers is provided to illustrate the potential for use and as an indication of both benefits and limitations that may be reached by using C_2H_4-based technology.

4.3.1 Tomato

The use of $KMnO_4$–based C_2H_4 scavengers has also shown good results in tomatoes, regarding quality maintenance during storage. Mujtaba et al. (2014) found that packaging 'Rio Grandi' tomato into PE bags together with a $KMnO_4$–based C_2H_4 scavenger can decrease SSC/ascorbic acid increment, induce TA to increase and retard lycopene

biosynthesis, without effects on fruit pH. Moreover, the use of a $KMnO_4$–based C_2H_4 scavenger in 'Chonto' tomato packaging can help to achieve lower weight and firmness losses and to slow SSC increment while TA is not affected (Salamanca et al., 2014).

4.3.2 Apple

$KMnO_4$–based C_2H_4 scavengers within apple packages at low storage temperature (0-4 ºC) have shown positive effects on quality parameters, being effective to delay the maturation process and then, prolonging its shelf life up to 8 months (Brackmann et al., 2015). Particularly, in 'Gala', 'Royal Gala', 'Golden Delicious' and 'Brookfield' cultivars, the incorporation of a $KMnO_4$–based C_2H_4 scavenger into the package has been shown to decrease pulp firmness loss and to delay shell yellowing. On the other hand, TA and SSC behaviours throughout the ripening process depend on the variety in question. Therefore, $KMnO_4$ effects on TA and SSC parameters are different in each variety. The latter fact may be explained since each variety has its unique characteristics. For example, the storage of 'Golden Delicious' apple under MAP conditions together with a $KMnO_4$ scavenger at low temperature led to a lower TA decrease and a lower SSC accumulation (Sardabi et al., 2014). Meanwhile, the TA decrease in the 'Gala' variety was delayed, while SSC was not affected (Brackmann et al., 2015; do Amarante & Steffens, 2009a). The opposite effect was observed in 'Royal Gala' apple being the SSC increase minimised while the TA behaviour was unaffected (do Amarante & Steffens, 2009b). In general, it can be concluded that $KMnO_4$–based C_2H_4 scavengers are a useful tool to reduce flavour changes or variations in sugars and free organic acid contents in apple fruit throughout storage at low temperatures.

4.3.3 Banana

Very good results have been found using $KMnO_4$–based C_2H_4 scavengers as a tool to delay banana ripening, especially for long-distance transportation. Such scavenger incorporation inside packages, storage rooms or banana allows to delay the shell yellowing process by delaying the chlorophyll degradation process, reduce weight loss and slow the softening process throughout the storage (García et al., 2012; Santosa et al., 2010; Tourky et al., 2014; Zewter et al., 2012).

As mentioned above, the TA and SSC changes are different depending on the characteristics of the product. In this sense, several authors pointed out that both TA and SSC factors tended to increase throughout the storage period of banana fruit (Santosa et al., 2010; Tourky et al., 2014; Zewter et al., 2012). Meanwhile, García et al. (2012) found that SSC increased while TA tended to decrease during the baby banana storage period.

However, in general, it has been observed that changes in TA and SSC are delayed when a $KMnO_4$-based material is incorporated into the banana packages regardless of whether the TA/SSC tended to increase/decrease (García et al., 2012; Santosa et al., 2010; Tourky et al., 2014; Zewter et al., 2012).

The banana pulp/peel ratio is a quality parameter that indicates differential changes in the moisture content of skin and pulp. This parameter tends to increase throughout the maturation process due to a differential change in osmotic pressure driven by the sugars increase in the pulp (Tourky et al., 2014). Nevertheless, Chauhan et al. (2006) reported that the pulp/peel ratio changes in 'Pachbale' bananas can be delayed if the fruit is packaged into a PE bag together with a $KMnO_4$–based C_2H_4 scavenger (5 g of scavenger per kg of fruit) and stored 18 days at 13 ºC. Similarly, 'Williams' banana stored in PE scavenger (20 g of $KMnO_4$ per 3 hands) showed bags together with a $KMnO_4$–based C_2H_4 a slight delay in the increase of pulp/peel ratio during 45 days at 20 ºC (Zewter et al., 2012). Nevertheless, the incorporation of a similar C_2H_4 scavenger tool inside a 'Raja Bulu' banana package (approximately 60 g of scavenger per kg of fruit) did not affect the pulp/peel ratio during 18 days at 27–30 ºC (Santosa et al., 2010).

Based on the above, $KMnO_4$–based C_2H_4 scavengers (in the form of sachets) are a potential tool in conjunction with the MAP technique to preserve the green life of banana during transportation. In this sense, Wills & Golding (2015) reported that the green life of 'Cavendish' bananas may be increased by removing C_2H_4 from the surrounding atmosphere of the fruit. For instance, changing the C_2H_4 concentration of 'Cavendish' banana atmosphere from 1.0 to 0.01 µL L^{-1} can result in a green life increase of about 27 days at 15 ºC, 17 days at 20 ºC and 11 days at 25 ºC.

4.3.4 Mango

The $KMnO_4$–based C_2H_4 scavenger effects have been also studied on mangoes. Ezz & Awad (2011) studied its effects on 'Hindi Basennara' and 'Alphonse' mangoes packaged under MAP conditions and stored at 8 ºC. The results showed fewer weight losses in both mango varieties, but no effect on firmness loss was observed. Similarly, Jeronimo et al. (2007) studied the effect of $KMnO_4$–based C_2H_4 scavengers on 'Tommy Atkins' mangoes at 13 ºC. However, no significant effect was observed on fruit firmness loss nor weight loss. At the end of the aforementioned studies, higher TA/ascorbic acid values and lower SSC were observed in the three studied mango varieties regarding that fruit packed without an C_2H_4 scavenger tool. Furthermore, Jeronimo et al. (2007) observed that C_2H_4 removal from the packaging reduced the fruit metabolism resulting in lower SSC and TA changes. Hence,

C_2H_4 scavengers are an effective tool to complement the MAP for maintaining the quality of mango fruit.

4.3.5 Other climacteric fruit

$KMnO_4$–based C_2H_4 scavenger effects have been also evaluated on other climacteric fruit such as papaya, quince fruit, fig, kiwi, sapote and sugar apple. Particularly, the incorporation of a $KMnO_4$–based C_2H_4 scavenger inside the 'Sunrise Golden' papaya package can help to reduce pulp consistency loss and the SSC increment, in addition to minimising peel colour changes (Silva et al., 2009). Based on similar observations, Bal & Celik (2010) reported that the 'Hayward' kiwi maturity process can be delayed by fruit packaging in conjunction with a $KMnO_4$–based C_2H_4 scavenger, which showed to be helpful to decrease firmness loss and TA changes, delay SSC increment, and to delay the chlorophyll degradation process.

Although a lower β–carotene content was observed by incorporating a $KMnO_4$ scavenger into the packaging of 'Isfahan' quince fruit, less firmness loss was observed (Akbari & Ebrahimpour, 2014). Meanwhile, SSC increment, TA decrease, weight losses and firmness losses can be delayed during the storage of 'Kallipati' sapote by using $KMnO_4$–based C_2H_4 scavengers (Bhutia et al., 2011). In sugar apple fruit, lower weight loss, lower SSC and TA increase, and a mild pH decrease were found after the incorporation of $KMnO_4$–based C_2H_4 scavengers (Chaves et al., 2007).

As can be seen from previously reported studies, the application of $KMnO_4$ scavengers in climacteric fruit packaging has mainly resulted in positive effects regarding quality maintenance. Nevertheless, some studies have not reported significant effects after the incorporation of a $KMnO_4$–based scavenger into the packaging. Sá et al. (2008) did not find significant C_2H_4 removal effects on melon. In addition, only a slight decrease in colour changes and a reduction of ascorbic acid biosynthesis was observed in guava fruit after the incorporation of $KMnO_4$–based C_2H_4 scavenger into the package (El-Anany & Hassan, 2013). Therefore, these studies suggest that this postharvest technique is not completely justified in guava and melon, although more research is needed to elucidate these issues.

4.3.6 Non-climacteric produce

Few significant information concerning $KMnO_4$–based C_2H_4 scavenger effects on non–climacteric products is available. Nonetheless, good results have been found. For instance, cherry storage in conjunction with a $KMnO_4$ scavenger resulted in fewer weight and firmness losses, while a delay in both SSC and TA changes was also observed (Emadpour,

Ghareyazie, et al., 2009). The ‘Precoce de Itaquera’ loquat shelf life was extended with the incorporation of a $KMnO_4$–based C_2H_4 scavenger into the package (de Campos et al., 2007). In another study on ‘Teresópolis Gigante’ cauliflower, it was possible to delay the chlorophyll degradation process by using an C_2H_4 scavenger (Brackmann et al., 2005). Furthermore, the ‘Marathon’ broccoli softening process was delayed when it was stored together with a sachet containing $KMnO_4$ (DeEll et al., 2006). As can be noted, $KMnO_4$–based C_2H_4 scavengers seem to be a useful tool to delay senescence processes of non-climacteric produce, but there is an insufficient body of trials to speculate on the potential of the technology on such produce.

OBJECTIVES

1 OBJECTIVES

1.1 GENERAL OBJECTIVE

The General Objective was to develop C_2H_4 remover tools intended to be used in active packaging systems to maintain postharvest quality attributes and prolong the shelf-life of fresh and minimally processed fruit and vegetables.

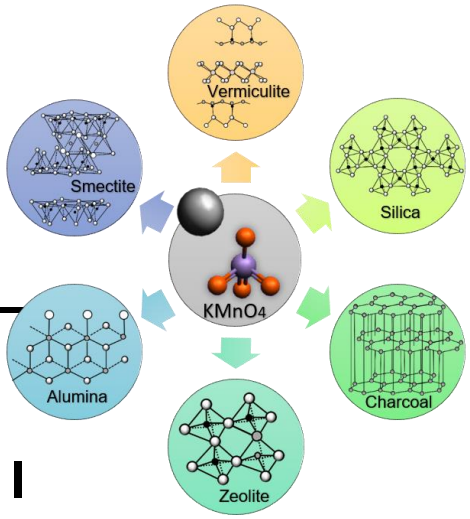
1.2 SPECIFIC OBJECTIVES

a. To develop innovative C_2H_4 scavenger tools using $KMnO_4$ as the active agent and treated porous minerals (i.e. montmorillonite and sepiolite), as well as to physicochemically characterize the developed tools.

b. To evaluate the ability of a prepared $KMnO_4$-loaded acid-treated montmorillonite to reduce the in-package C_2H_4 concentration, and to determine the $KMnO_4$-loaded montmorillonite effect on the main physical, physicochemical, safety and sensory quality characteristics of fresh blueberry fruit packed in a modified atmosphere and stored at 2 (recommended storage temperature) and 10 °C (usual storage temperature during retail).

c. To evaluate the ability of a prepared $KMnO_4$-loaded acid-treated sepiolite to reduce the in-package C_2H_4 concentration, and to study the efficiency of the $KMnO_4$-loaded sepiolite to retain the main physical, physicochemical and sensory quality characteristics of fresh apricot fruit during storage in modified atmosphere packaging at 2 °C (recommended storage temperature) and under air packaging conditions at 15 °C (unproper storage temperature during retail).

d. To prepare active sachets carrying an C_2H_4 scavenger material consisting of a $KMnO_4$-loaded sepiolite with or without the antimicrobial agent thymol and evaluate its antifungal activity both *in vitro* against *Botrytis cinerea* and *in vivo* on artificially infected cherry tomatoes. Furthermore, to assay the prepared active sachet's potential as an active packaging tool to maintain the overall quality of fresh cherry tomatoes during storage at 11 °C (recommended storage temperature) and after 3 additional days at 22 °C (simulation of commercialization period).



CHAPTER I

Development of Innovative Ethylene Scavengers Based on Potassium Permanganate Supported on Modified Clays

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CHAPTER I. DEVELOPMENT OF INNOVATIVE ETHYLENE SCAVENGERS BASED ON POTASSIUM PERMANGANATE SUPPORTED ON MODIFIED CLAYS

I.1 Introduction

Conventional C_2H_4 removal techniques include air ventilation, ethylene adsorbers, chemical oxidizers, catalytic oxidizers and hypobaric storage (Brecht, 2019; Li et al., 2016). However, these technologies may face several drawbacks such as insufficient C_2H_4 removal capacity, high production costs, the requirement of heating systems, poor selectivity, inability for working at low temperatures, dependence on high amounts of energy and generation of unwanted by-products (Cisneros et al., 2019; Hu et al., 2019).

Those C_2H_4 scavengers based on $KMnO_4$ are the most implemented technologies in postharvest environments because of the high ERR of $KMnO_4$ (Brecht, 2019; Pathak et al., 2017). $KMnO_4$ is a powerful, feasible, relatively inexpensive, and vigorous 'green' oxidation agent that has demonstrated high efficiency for chemically oxidizing C_2H_4, even at low temperatures (Álvarez-Hernández et al., 2019; Dash et al., 2009; Li et al., 2016). The C_2H_4 oxidation pathway involves the permanganate ion (MnO_4-; which has a tetrahedral geometry with extensive μ-bonding) reacting with the double bond of C_2H_4 and generating CO_2 and H_2O as the main end-products (Álvarez-Hernández et al., 2018; Dash et al., 2009).

In order to enhance selectivity and reactivity, $KMnO_4$ is normally loaded over an inert solid porous support and used as a heterogeneous oxidant (Dash et al., 2009). This approach often exploits the ability of certain materials to adsorb C_2H_4 (Pathak et al., 2017). Activated alumina, zeolite, silica gel, activated carbon and vermiculite are most frequently applied as $KMnO_4$ supports as previously reviewed (Álvarez-Hernández et al., 2018). These adsorbers usually trap C_2H_4 molecules by either ion-quadrupole interaction or Van der Waals force (Li et al., 2016). However, the C_2H_4 scavenger performance is influenced by several factors, mainly those related to the textural and structural features of the support materials (Álvarez-Hernández et al., 2018). Particularly, the C_2H_4 removal efficiency of $KMnO_4$-based scavengers is strongly affected by the surface area of the support, showing a positive correlation (Spricigo et al., 2017). Thus, suitable supports featuring a large surface area are essentials to obtain effective $KMnO_4$-based C_2H_4 scavengers with high oxidative activity.

Clay minerals are hydrous aluminium phyllosilicates of small particle size (particles smaller than 2 μm) that have attracted high attention because of their availability, low cost and environmental compatibility, but especially because they can be tailored for different purposes (Avalos et al., 2009; Hwang et al., 2019). Compared with other clay minerals, The

clay MMT presents significant potential advantages including higher cation exchange capacity, larger surface area and excellent swelling properties, while it is more abundant in soil (Alamudy & Cho, 2018; Kaur & Kishore, 2012). Therefore, MMT could be highly effective as sustained support for C_2H_4 removal purposes.

The MMT belongs to the smectite group and has a 2:1 silicate layer structure comprising an alumina octahedral sheet located between two silica tetrahedral sheets —in which SiO_4 tetrahedrons are arranged in a hexagonal mesh network (Alver, 2017). Due to the chemical nature and extent of its surface, as well as to Van der Waals, ion-dipole, and/or dipole-dipole interactions, MMT can bind a large number of organic molecules (Ibrahim et al., 2018; Kaur & Kishore, 2012). In fact, MMT exhibits considerable good C_2H_4 adsorption properties (Alver, 2017). Additionally, the surface area of MMT along with its adsorption capacity and affinity towards C_2H_4 can be even improved further by acid activation (Alver & Sakizci, 2012; Medhi & Bhattacharyya, 2017).

To date, MMT supporting $KMnO_4$ has been used for promoting the oxidation of various organic compounds including imidazolines, alcohols, sulphides, thiols, alkylarenes, and alkenes (Choudary et al., 1991; Mohammadpoor-Baltork & Abdollahi-Alibeik, 2005; Ahmad Shaabani et al., 2002, 2004). Nevertheless, its application for C_2H_4 removal has been neglected and less studied.

This study deals with the development of an effective $KMnO_4$-based C_2H_4 scavenger supported by MMT. In order to obtain suitable support for enhancing the C_2H_4 oxidative activity of $KMnO_4$, different preparation methods were performed and their effect on structural and morphological features of MMT was studied. The developed C_2H_4 scavenger was further subjected to C_2H_4 removal measurements and its ERR was compared with a commercially available $KMnO_4$-based C_2H_4 scavenger. To the best of our knowledge, this is the first report evaluating the C_2H_4 scavenging activity of $KMnO_4$ supported on MMT.

I.2 Material and methods

I.2.1 Materials

Sodium MMT (cation exchange capacity of 92 cmol(+) kg^{-1}) was obtained from Southern Clay Products Inc. (Gonzales TX, USA). The reagents $KMnO_4$ and hydrochloric acid (HCl, 36–38 %) were supplied by Sigma–Aldrich (Germany) and all solutions were prepared by using double-distilled H_2O. A commercial C_2H_4 scavenger (Bi–On® R12; C_2H_4 removal capacity of 4.5 ± 0.5 L kg^{-1}) comprising a natural zeolite as $KMnO_4$ support was provided

by Bioconservacion S.A. (Barcelona, Spain). The powder XRD patterns of both the pristine MMT and the commercial C_2H_4 scavenger are shown in Figure I.1 and I.2, respectively.

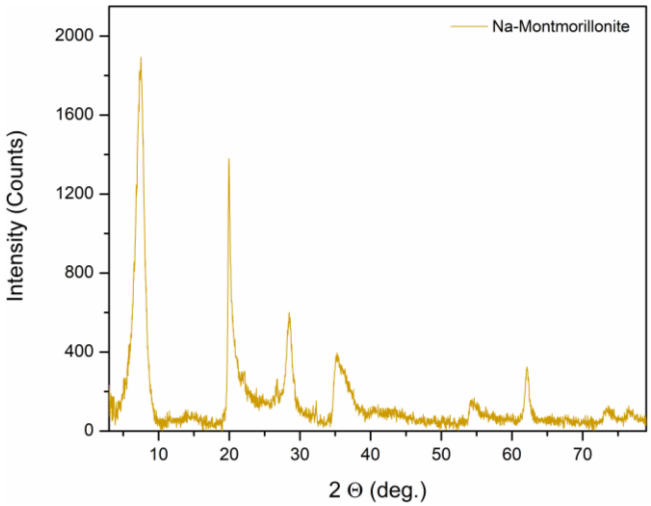


Figure I.1. X-ray diffraction pattern of pristine montmorillonite (source: Own elaboration).

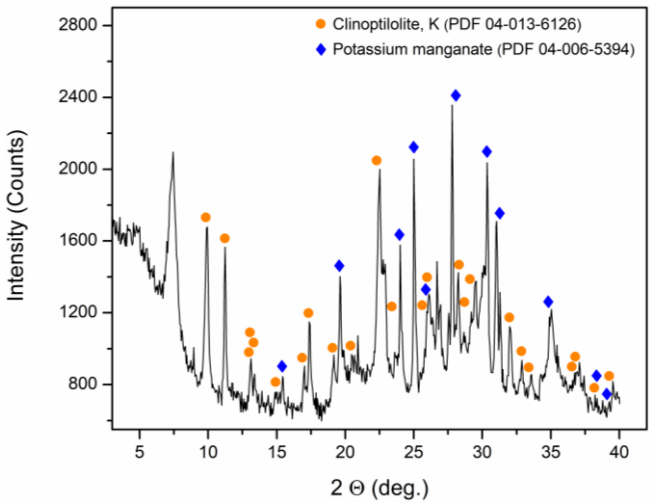


Figure I.2. X-ray diffraction pattern of a commercial $KMnO_4$–based C_2H_4 scavenger (Bi–On® R12, Bioconservacion S.A., Barcelona, Spain) (source: Own elaboration).

I.2.2 Preparation of potassium permanganate-loaded montmorillonite

Pristine MMT samples were treated according to the method previously described by Avalos et al. (2009), with some modifications, as follows: 1) a swelling process was performed by mixing 50 g of dry MMT with hot distilled H_2O (1 L) and mechanically stirring overnight; 2) then, the swollen MMT was treated with a 0.025 M HCl solution (0.5 L) under stirring at 80 ºC for 2 h; 3), and subsequently the acid slurry was centrifugated and washed with hot H_2O several times until the precipitate was found at neutral pH; 4) and finally the neutral precipitate was rinsed with absolute ethanol and then dried overnight at 60 ºC. The resulting acid-treated MMT was denoted as AcMt. Similarly, a second MMT sample was treated as

described above, but the acid activation process (step 2) was not carried out. Thus, after the swelling process was performed, the swollen MMT was centrifuged and washed with hot H_2O. Following this, the obtained precipitate was rinsed with absolute ethanol and dried at 60 ºC. The final dried MMT is hereinafter referred to as SwMt.

Finally, each pre-treated MMT sample was subjected to the swelling process again (Step 1), and then a $KMnO_4$ saturated solution —in $KMnO_4$-MMT ratio of 0.1 *w/w*— was added as previously reported (Álvarez-Hernández et al., 2019). Then, the $KMnO_4$-MMT slurries were left to dry at 60 ºC, and ground in a ball mill. The obtained $KMnO_4$-loaded samples are hereinafter referred to as AcMt+$KMnO_4$ and SwMt+$KMnO_4$. Additionally, a dry blend was also prepared in a $KMnO_4$/MMT ratio of 0.1 using a ball-mill and denoted as Mt+$KMnO_4$.

The performed treatments and sample identification are summarized in Table I.1. Before the experimental procedure, all the samples were dried at 60 ºC overnight and stored in a desiccator.

Table I.1. Sample identification and description of treatments (source: Own elaboration).

Nomenclature	Treatment description	$KMnO_4$-MMT ratio
Pristine Mt	No treated MMT	-
SwMt	MMT swelled in water	-
AcMt	MMT swelled in water and treated with HCl	-
Mt+$KMnO_4$	Dry blend of MMT and $KMnO_4$	0.1
SwMt+$KMnO_4$	SwMt impregnated with $KMnO_4$-solution	0.1
AcMt+$KMnO_4$	AcMt impregnated with $KMnO_4$-solution	0.1

MMT: montmorillonite

I.2.3 Characterization of the prepared samples

The WAXS patterns were collected using a diffractometer (SAXSess mc^2; Anton Paar GmbH, Graz, Austria), which was operated with a line collimated CuKα radiation (λ=0.1542 nm) and an exposition time of 0.5 min. The working voltage and the applied current were 40 kV and 50 mA, respectively. The d-spacing values between layers of prepared samples were determined by the Bragg's law:

$$n\lambda = 2d\,sin\theta \quad (24)$$

The $KMnO_4$ incorporation into the MMT structure was analysed through TEM (Philips Tecnai 12, Amsterdam, The Netherlands) operated at 120 kV. Samples for TEM were previously dispersed in distilled H_2O (5 mg mL^{-1}) using a 5 min ultrasound bath. Subsequently, one drop of a diluted (1:10) sample dispersion was mounted on a nickel grid (formvar/carbon film 200 mesh, nickel; Electron microscopy sciences, Hatfield PA, USA).

The surface morphology of all samples was observed through SEM (Hitachi S–3500N, Tokyo, Japan). The aggregate sizes of the $KMnO_4$–loaded MMT samples were analysed using FE-SEM (Hitachi SU8010, Tokyo, Japan). Before microscopic observations, dried samples were mounted on aluminium discs and coated with gold in a sputter coater (model SC7640, Quorum Technologies, East Sussex, UK). Textural properties of the $KMnO_4$-loaded MMT samples were obtained from the N_2 adsorption/desorption isotherms, which were measured at –196 ºC (Quadrasorb-evo; Quantachrome Instruments, Boynton Beach FL, USA). Before adsorption-desorption measurements, samples were degassed under vacuum at 200 ºC for 8 h. Specific surface areas were determined by the multipoint BET method.

The TG analyses of the $KMnO_4$-loaded MMT samples, as well as the pure $KMnO_4$ reagent, were performed on a thermal analyser (Pyris 6 PerkinElmer TGA 4000; Waltham MA, USA) under constant heating and flow rates of 20 ºC min^{-1} and 20 mL min^{-1}, respectively. Samples (7.8-18.9 mg) were heated in flowing N_2 from 30 to 600 ºC and inflowing O_2 from 600 to 850 ºC.

I.2.4 Ethylene scavenger activity

I.2.4.1 Breakthrough experimentation

The C_2H_4 removal capacity was measured by breakthrough experiments, which were conducted in a flow-through system based on Terry et al. (2007), with some modifications. In brief, a $KMnO_4$-loaded MMT sample (1 g) was placed inside a borosilicate glass column (1 cm Ø; 24.5 cm length; 20 mL internal volume). The packed column was then sealed and connected to an C_2H_4-enriched gas stream (gas composition 5,000 µL L^{-1}, balanced with N_2; Praxair España, S.L.U., Madrid, Spain) at a flow rate of 140 mL min^{-1}. Outlet gas samples were analysed using a gas chromatograph (GC; 7820A series, Agilent Technologies, Santa Clara CA, USA), equipped with a flame ionisation detector and configurated as previously described (Álvarez-Hernández et al., 2019). For evaluating the temperature effect on the C_2H_4 scavenging activity, the breakthrough curves were recorded at fixed temperatures of 2, 10 and 22 °C. The effluent composition values were recorded

until the outlet C_2H_4 concentration reached the inlet above-specified concentration, and the total integrated C_2H_4 removal was then calculated.

I.2.4.2 Evaluation of ethylene removal rate

The ERR experiments were performed in a closed system according to Cao et al. (2015), with some adaptations. In brief, the $KMnO_4$-loaded MMT sample (0.1 g) was placed into a 20–mL hermetically sealed glass vial. Subsequently, a 1–mL C_2H_4 (5,000 µL L^{-1}; balanced with N_2) aliquot was injected into the vial, yielding an initial C_2H_4 concentration of approximately 116 µL L^{-1}. After injection, the vial was incubated at 22 °C and headspace gas samples (0.5 mL) were taken from the vial and analysed using a GC system as described above. The ERR of the assayed materials was expressed as the percentage difference between the initial and final C_2H_4 concentrations in the vial at each sampling time. The ERR of a common and effective $KMnO_4$–based C_2H_4 scavenger (Bi–On® R12, Bioconservacion S.A., Barcelona, Spain) was used as a commercial control. The $KMnO_4$ concentration on the developed scavenger was determined according to Wills and Warton (Wills & Warton, 2004).

I.3 Results and discussion

I.3.1 X-ray analyses

The measured WAXS diffractograms of the pristine, pre-treated and $KMnO_4$-loaded MMT samples are shown in Figure I.3. A main diffraction peak with a maximum at 8.3-8.8 ° was observed for all samples, without noteworthy differences in shape or position among samples. Particularly, the WAXS analyses revealed that the interlamellar distance of the pristine MMT (d-spacing=1.03 nm) was not affected by the performed treatments. Any remarkable change in the value of the d_{001} basal plane occurred after the addition of $KMnO_4$, indicating only very low interactions between the clay matrix and the $KMnO_4$ compound. Thus, it can be assumed that $KMnO_4$ was not intercalated into the MMT galleries, but it was attached to the external surface of the aluminosilicate layers (Liu et al., 2009).

I.3.2 Morphological characterization

The effects of preparation conditions were also analysed employing TEM. The dark lines observed in all prepared samples (Figure I.4) corresponds to the cross-section of the MMT aluminosilicate layers (Mittal, 2009). Both the pristine MMT and the pre-treated samples revealed dispersed layers but in general, all the samples showed an agglomerated morphology, even after the addition of $KMnO_4$. Therefore, the WAXS patterns did not

evidence substantial differences among samples concerning the basal plane reflection (d_{001}).

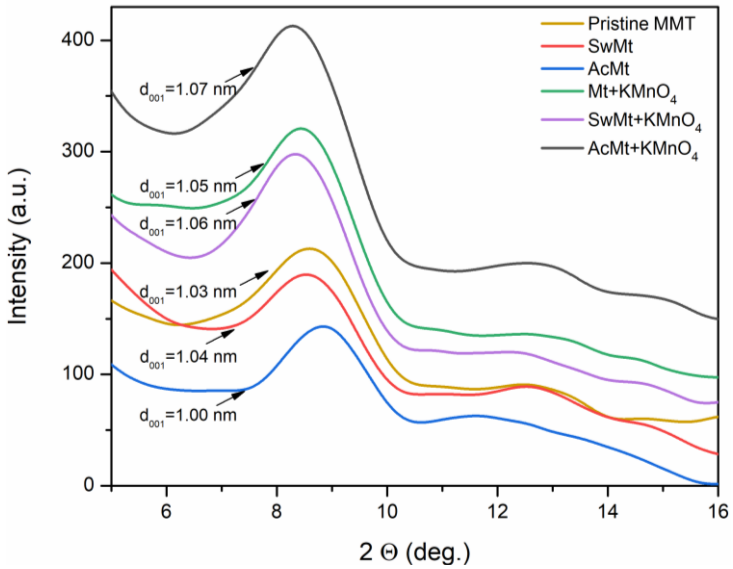


Figure I.3. Wide-angle X-ray scattering patterns of pristine (Pristine MMT), swollen (SwMt) and acidified montmorillonite (AcMt), and of their corresponding $KMnO_4$-loaded form (Mt+$KMnO_4$, SwMt+$KMnO_4$ and AcMt+$KMnO_4$, respectively). d_{001}: spacing between (001) planes (basal spacing) (source: Own elaboration).

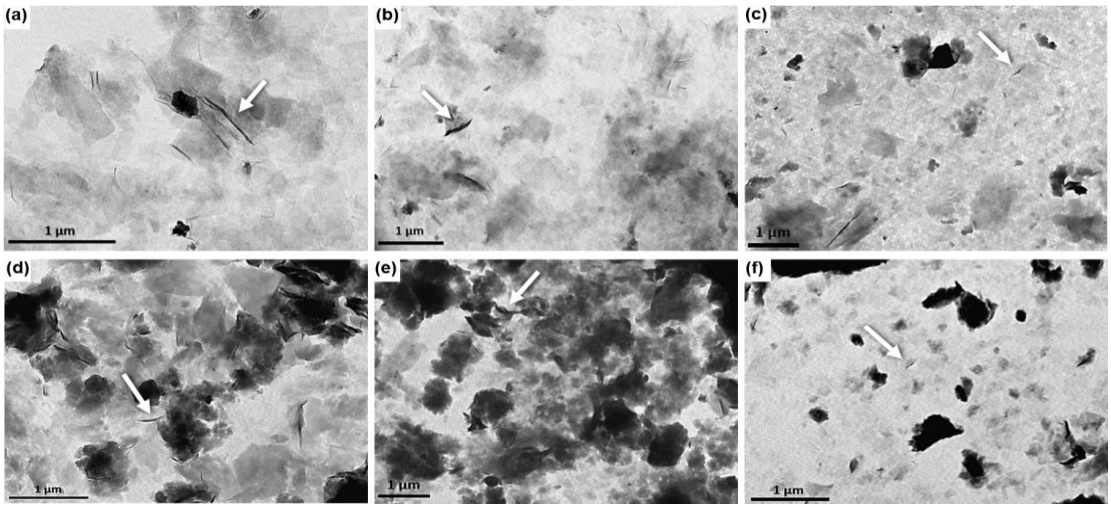


Figure I.4. Transmission electron microscopy images of pristine montmorillonite (a), swollen montmorillonite (SwMt; b) and acidified montmorillonite (AcMt; c) montmorillonite samples, and of their respective $KMnO_4$-loaded form: Mt+$KMnO_4$ (d), SwMt+$KMnO_4$ (e) and AcMt+ $KMnO_4$ (f). The arrows show the cross-section of Mt silicate layers (source: Own elaboration).

Among the pre-treated samples, the largest flakes were observed for the pristine MMT (Figure I.4a), whereas the smallest flakes were observed for the AcMt sample (Figure I.4c). The small flakes observed for the AcMt sample may be attributed to aluminium leaching from the octahedral sheet as a result of the acid treatment (Medhi & Bhattacharyya, 2017). On the other hand, from WAXS analyses and TEM images (Figure I.4d, e, f), it can be

deduced that the $KMnO_4$ was physically adsorbed on the external surface of the MMT. Besides, it was evident that the AcMt particles were more homogeneous in terms of size, in comparison with the pristine MMT and SwMt samples.

From SEM images (Figure I.5), a variation on the MMT morphology after the swelling and acidification processes was observed, as well as after the $KMnO_4$ loading. The surface of the pristine MMT showed some deposited granules (Figure I.5a), whereas that of the SwMt sample was found to be smooth (Figure I.5b). Moreover, a highly ordered layered morphology was distinguished for the SwMt sample. The latter observations suggest that the pristine MMT had some impurities, which were removed by the swelling process.

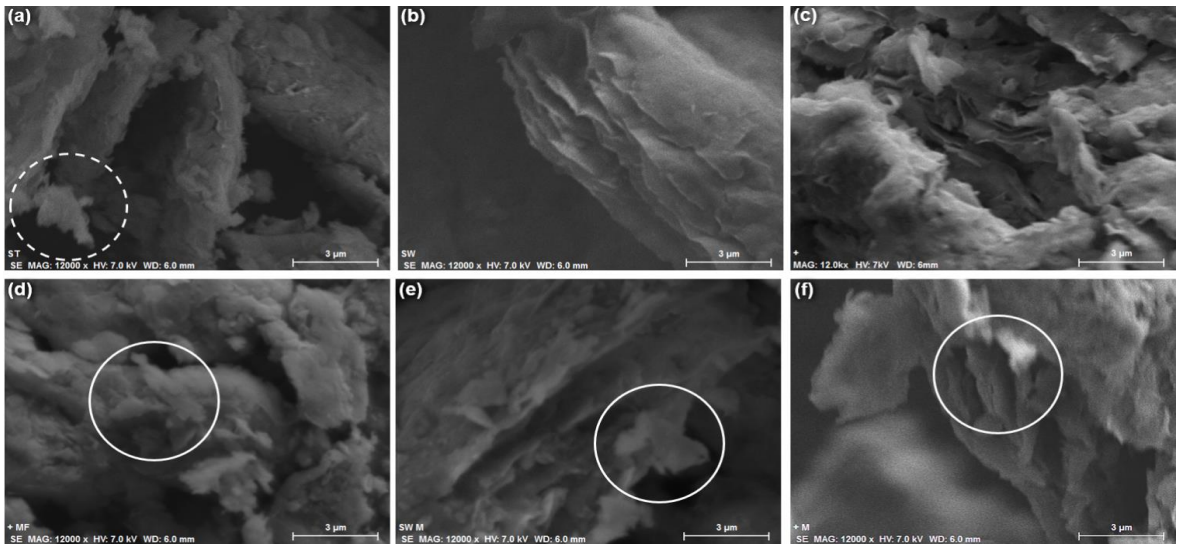


Figure I.5. Scanning electron microscopy images of pristine montmorillonite (a), swollen montmorillonite (SwMt; b) and acidified montmorillonite (AcMt); c) montmorillonite samples, and of their respective $KMnO_4$-loaded form: Mt+$KMnO_4$ (d), SwMt+$KMnO_4$ (e) and AcMt+$KMnO_4$ (f) at 12,000× magnification (accelerating voltage: 7 kV). The dotted circle indicates possible impurities present in the sample, and the solid circles show deposition of probably permanganate salt particles (source: Own elaboration).

On the other hand, the AcMt sample evidenced layers tightly stacked together and a rough surface (Figure I.5c). Similarly, Hadjltaief et al. (2017) observed a morphological change in MMT upon acid treatment: from a smooth to a porous surface. The SEM images of the $KMnO_4$–loaded samples (Figure I.5d, e, f) showed deposition of substances on the MMT surface, which probably corresponds to permanganate salt particles.

Furthermore, both Mt+$KMnO_4$ and SwMt+$KMnO_4$ showed similar large aggregates of uneven particle sizes, whereas AcMt+$KMnO_4$ revealed smaller aggregates (Figure I.6). Moreover, the AcMt+$KMnO_4$ aggregates evidenced a rough surface (Figure I.6c). Taking into account the TEM insights, it is clear that the lamellar structure of the pristine MMT was disrupted by acid treatment. In agreement, Angaji et al. (2013) observed that the MMT

morphology changed from large layers to smaller layers upon acid treatment and that the size of MMT aggregates is reduced as the acid concentration is increased.

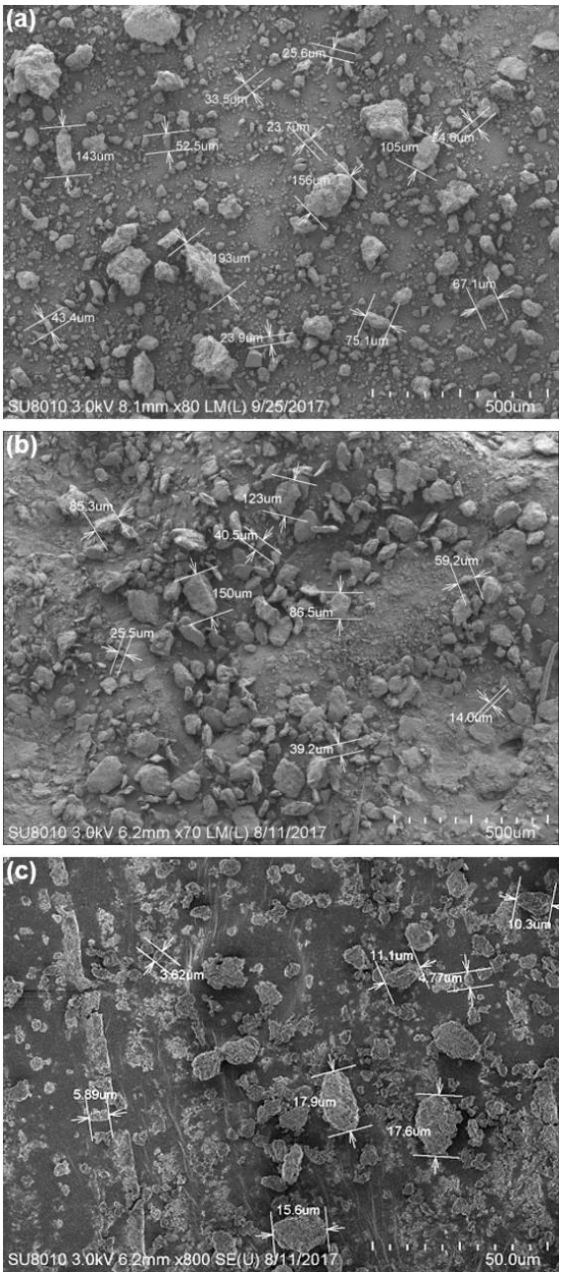


Figure I.6. Scanning electron microscopy images of $KMnO_4$–loaded montmorillonite aggregates: Mt+$KMnO_4$ (a), swollen Mt+$KMnO_4$ (SwMt+$KMnO_4$) (b) and acidified Mt+$KMnO_4$ (AcMt+$KMnO_4$) (c) at a magnification of 80×, 70× and 800×, respectively (accelerating voltage: 3 kV) (source: Own elaboration).

I.3.3 Specific surface area

The N_2 adsorption-desorption isotherms of the $KMnO_4$–loaded MMT samples are shown in Figure I.7. According to the IUPAC classification, the shape of N_2 adsorption isotherms of the hereby evaluated samples corresponds to Type II behaviour with a type H3 hysteresis

loop (Sing, 1985). Such observed behaviour is characteristic of mesoporous solids, often associated with the lamellar structure and slit-shaped pores such as MMT (Hwang et al., 2019). The BET surface area of the Mt+$KMnO_4$, SwMt+$KMnO_4$ and AcMt+$KMnO_4$ samples were 40.84, 45.47 and 91.70 m^2 g^{-1}, respectively. As observed, the AcMt+$KMnO_4$ sample showed the highest surface area. Correlating these results with TEM and SEM observations, the morphology resulting from the acid treatment gives rise to an enhanced surface area. Alver & Sakizci (2012) attributed the increased surface area to the removal of impurities, the substitution of exchangeable cations with H_2 ions (H^+) and the disaggregation of particles.

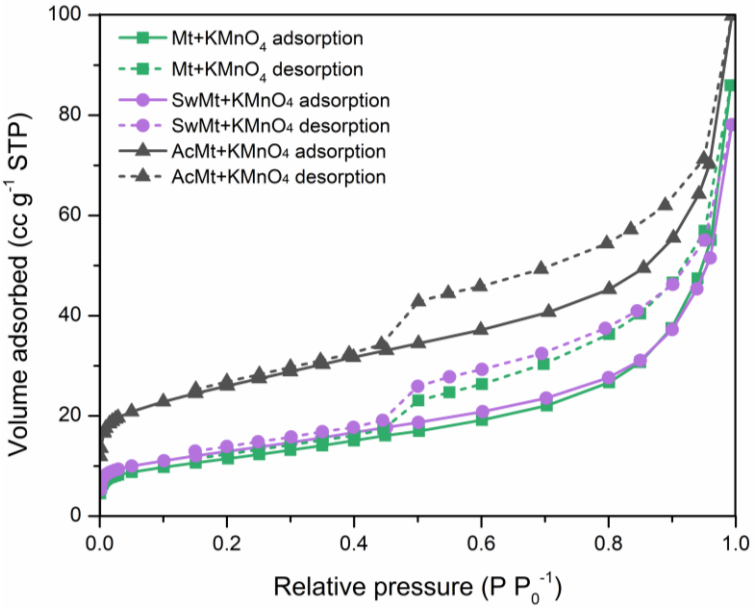


Figure I.7. N_2 adsorption-desorption isotherms of $KMnO_4$-loaded pristine (Mt+$KMnO_4$), $KMnO_4$-loaded swollen (SwMt+$KMnO_4$) and acidified (AcMt+$KMnO_4$) montmorillonite samples (source: Own elaboration).

I.3.4 Thermal properties

In line with the results obtained up to this point, the amount of $KMnO_4$ fixed on the surface of the nanoclay particles was determined by TG analysis. Results showed that $KMnO_4$ degradation occurs close to 300 °C (Figure I.8a). Among the $KMnO_4$-loaded samples, the highest mass loss as a function of temperature was shown by the AcMt+$KMnO_4$ sample, with a mass loss of approximately 4 %.

Furthermore, the interaction degree between MMT and $KMnO_4$ as a function of the treatment to which the samples were subjected can be observed through the DTG plots (Figure I.8b). The DTG curves evidenced that there were no relevant differences among samples regarding the temperature of maximum $KMnO_4$ loss. The latter confirmed that the

Mt-$KMnO_4$ interaction arises exclusively through the adsorption of such agent on the clay surface.

Thus, in conjunction with the previous characterization insights, it can be concluded that the $KMnO_4$ was deposited on the external surface of the MMT agglomerates. In agreement, the higher surface area obtained after the acid treatment allowed higher $KMnO_4$ retention on the MMT surface, in comparison with that shown by the pristine and swollen MMT samples. Overall, the results suggested acid-treated MMT as the most suitable support for $KMnO_4$ loading.

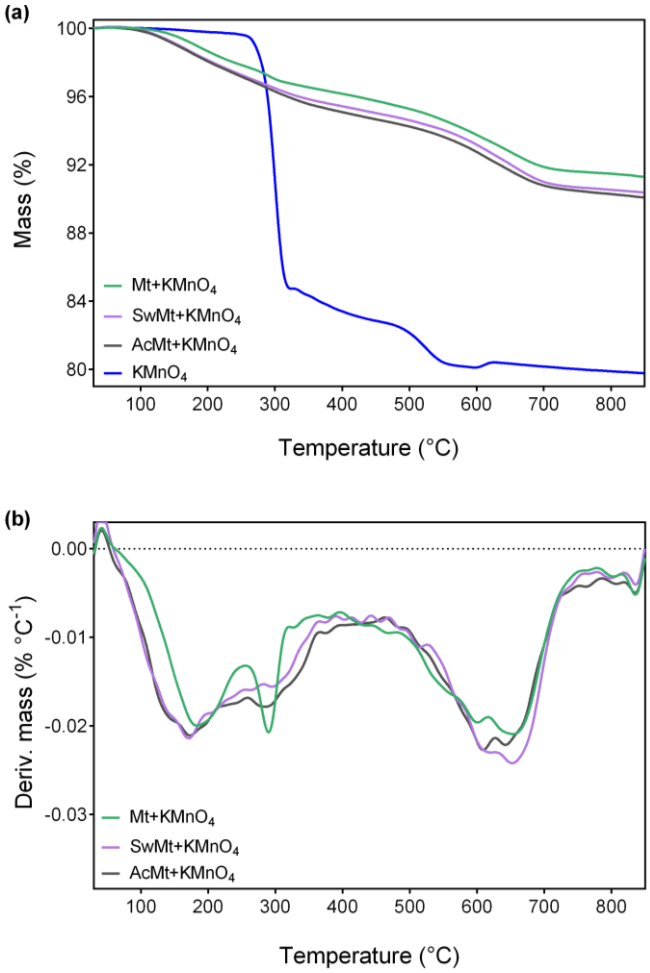


Figure I.8. Thermogravimetric curves of $KMnO_4$-loaded pristine (Mt+$KMnO_4$), $KMnO_4$-loaded swollen (SwMt+$KMnO_4$) and $KMnO_4$-loaded acidified (AcMt+$KMnO_4$) montmorillonite samples (a), and the corresponding derivative thermogravimetry plots of the $KMnO_4$–loaded montmorillonite samples (b) (source: Own elaboration).

I.3.5 Ethylene scavenging activity

Due to high surface area, the AcMt+$KMnO_4$ sample was selected and its C_2H_4 removal performance was evaluated at 2, 10 and 22 °C. Such temperatures comply with the ideal (in non–chilling sensitive produce), maximum and misused suggested storage conditions,

respectively, during the perishable produce supply chain (Artés et al., 2001; Aung & Chang, 2014). The relationship between C_2H_4 concentration and time followed a logarithmic behaviour regardless of the temperature factor (Figure I.9). The AcMt+$KMnO_4$ sample had a high potential to be used as a C_2H_4 scavenger. The C_2H_4 removal activity of the AcMt+$KMnO_4$ sample was strongly affected by temperature, showing a maximum removal capacity of 10.5, 16.4 and 12.6 L kg^{-1}, at 22, 10 and 2 °C, respectively.

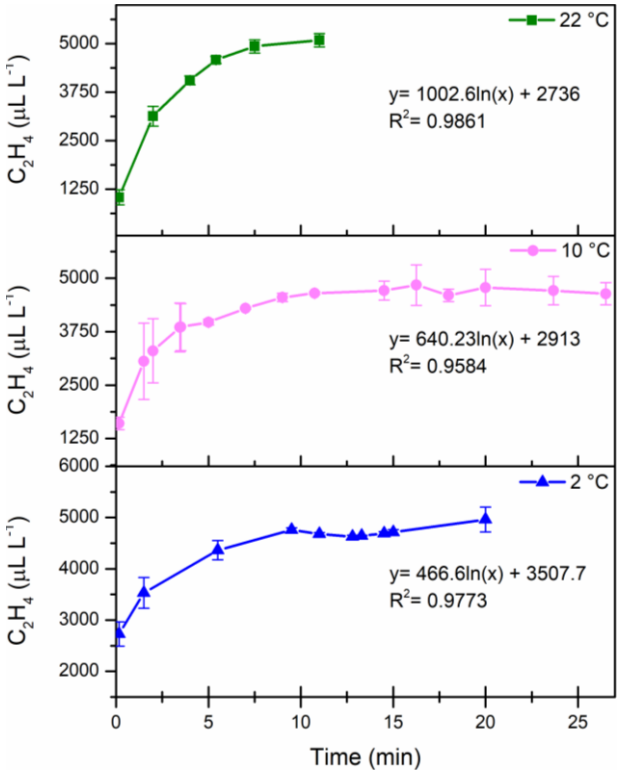


Figure I.9. C_2H_4 breakthrough measurements on the $KMnO_4$ supported acidified montmorillonite at 22, 10 and 2 °C (mean (n=3)±standard deviation) (source: Own elaboration).

Earlier, it was reported that the C_2H_4 scavenging effectiveness of both $KMnO_4$ crystals and $KMnO_4$–impregnated aluminium oxide is improved as the temperature increases (Lidster et al., 1985). In agreement, we observed that the maximum removal capacity increased from 2 to 10 °C. Following the kinetic theory model of gases, gas molecules move faster as the temperature increases and thence collisions between molecules and the container walls are more frequent (Grad, 1958). Therefore, when the temperature was increased from 2 to 10 °C, the contact between C_2H_4 molecules and the AcMt+$KMnO_4$ scavenger increased enhancing the C_2H_4 scavenging activity. However, when the temperature was increased up to 22 °C, the opposite trend was found. Specifically, the maximum C_2H_4 removal capacity exhibited by the AcMt+$KMnO_4$ sample decreased from 10 to 22 °C, being even lower than at 2 °C.

The variation in the C_2H_4 scavenging capacity at different temperatures could be associated with the kinetic energies of gas molecules and more precisely, with the critical temperature of C_2H_4 (9.4 °C). The increased C_2H_4 kinetic energies were favourable below and close to the Tc, but they were hostile above the Tc (Alver & Sakizci, 2012). In line with this, Hwang et al. (2019) suggested that complete alkene saturation in clays is just achieved at near-critical conditions. On the one hand, a combination of surface-C_2H_4 and C_2H_4-C_2H_4 interaction occurs at the beginning of the C_2H_4 adsorption process, but only mutual interaction of C_2H_4 molecules may occur with the increase in the surface coverage (Saini et al., 2010). Nevertheless, the possibility for C_2H_4 interactions is reduced when the temperature increases above the Tc and the surface-C_2H_4 interactions are weak. On the other hand, the absence of a vapour-liquid transition at supercritical conditions prevents C_2H_4 from completely occupying the pore space, but with the decrease in temperature the volume occupied by C_2H_4 increases (Hwang et al., 2019).

These findings not only highlight the importance of the support but also demonstrate that C_2H_4 adsorption properties of MMT remain after the $KMnO_4$ adsorption. Additionally, the observed behaviour makes evident that the C_2H_4 scavenging activity of the AcMt+$KMnO_4$ sample works by an C_2H_4 adsorption-oxidation mechanism. The maximum C_2H_4 removal capacity of the AcMt+$KMnO_4$ sample was 10.5 L kg^{-1} at 22 ºC, which is much higher than that claimed by the commercial $KMnO_4$-based C_2H_4 scavengers. For instance, Befresh$^+$ (Befresh Technology, S.L., Barcelona, Spain) and Bi-On® R12 (Bioconservacion S.A., Barcelona, Spain) are two of the commercial scavengers with the highest claimed C_2H_4 removal capacities: 6.5 and 4.5 L kg^{-1}, respectively (Álvarez-Hernández et al., 2019). The C_2H_4 removal effectiveness of the scavenger AcMt+$KMnO_4$ was also higher than that of C_2H_4 scavengers reported in the literature. In previous studies, an C_2H_4 removal capacity of 0.76 L kg^{-1} at 20 ºC was reached using $KMnO_4$–impregnated alumina beads (Wills & Warton, 2004), while a capacity of 4.16 L kg^{-1} at 20 ºC was reported using palladium–impregnated zeolite particles (Terry et al., 2007).

I.3.6 Ethylene removal rate evaluation

The ERR of the AcMt+$KMnO_4$ sample was evaluated against the commercial C_2H_4 scavenger Bi-On® R12 (Figure I.10). The AcMt–$KMnO_4$ sample was capable to remove up to 80 % of the injected C_2H_4 after 5 min of exposure, removing virtually 100 % of the C_2H_4 after 20 min. On the other hand, the commercial scavenger was just capable to remove 59 % of the C_2H_4 after 5 min of injection, 84 % after 10 min, and removed almost all the injected C_2H_4 just after 35 min. As previously commented, the C_2H_4 removal capacity of the AcMt+$KMnO_4$ sample was found to be 1.33 times higher than that claimed for the

commercial scavenger. In addition, Bi-On® R12 has a $KMnO_4$ concentration of 12 % (*w/w*) according to the supplier datasheet, whereas the corresponding value for the AcMt+$KMnO_4$ sample was found to be 8 % (*w/w*). Results showed that both scavengers were able to remove 100 % of the injected C_2H_4, irrespective of their C_2H_4 removal capacity and $KMnO_4$ content. However, it was accomplished at different times suggesting the ERR is mainly influenced by the $KMnO_4$ supports themselves.

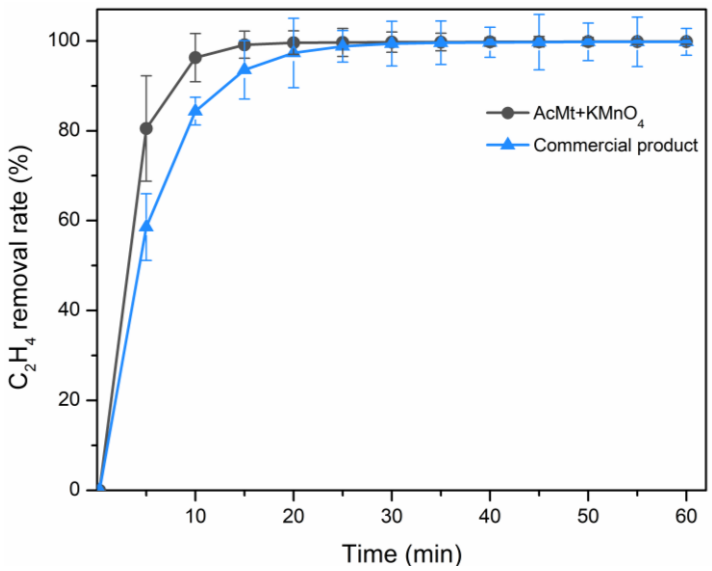


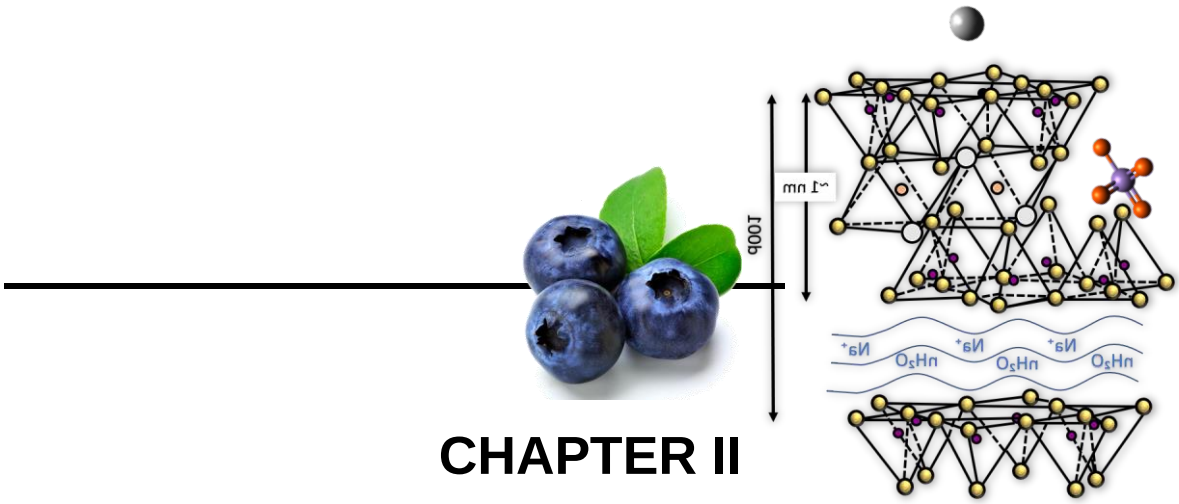
Figure I.10. Rate of C_2H_4 removal percentage of the $KMnO_4$ supported acidified montmorillonite (AcMt+$KMnO_4$) in comparison with a commercial $KMnO_4$–based C_2H_4 scavenger (Bi–On® R12) at 22 °C (mean (n=3)±standard deviation) (source: Own elaboration).

Previously, ERR as a function of the $KMnO_4$ concentration, chemical nature and size of the $KMnO_4$ support has been reported by Spricigo et al. (2017). The last authors found that silica and alumina nanoparticles loaded with $KMnO_4$ removed C_2H_4 more efficiently than their micrometric counterparts, whilst the alumina particles were more efficient than the silica ones. In the present study, the AcMt+$KMnO_4$ sample was shown to have a faster ERR than the commercial reference. The commercial scavenger Bi-On® R12 comprises a $KMnO_4$-loaded clinoptilolite (Figure I.2) supplied in pellet form (2.3–4 mm Ø The ERR of a common and effective $KMnO_4$–based C_2H_4 scavenger (Bi–On® R12, Bioconservacion S.A., Barcelona, Spain) was used as a commercial control.). Hence, the high C_2H_4 scavenging efficiency of the AcMt+$KMnO_4$ sample may be directly attributed to the physicochemical characteristics (e.g. micrometric size and irregular form) of the acid-treated MMT. These results evidence the acid-treated MMT as proficient $KMnO_4$ support to reach a high C_2H_4 removal activity.

I.4 Conclusions of this chapter

In the developed $KMnO_4$/MMT system, $KMnO_4$ possessed the oxidative C_2H_4 activity, while the acid-treated MMT demonstrated to be effective for promoting the C_2H_4 scavenging activity. The conditions under which the C_2H_4 scavenger was prepared greatly influenced the $KMnO_4$ loading and its final physical features as well. Higher surface area, smaller particle size and a rough morphology were obtained by acid treatment of MMT prior to $KMnO_4$ loading. Results showed that the MMT properties played a pivotal role in the C_2H_4 removal activity. Because the developed C_2H_4 scavenger showed a temperature-dependent saturation, it was suggested that the C_2H_4 adsorption properties of MMT were preserved after $KMnO_4$ loading.

The prepared $KMnO_4$-loaded MMT was able for efficiently removing C_2H_4, working even better at low temperatures (10 and 2 °C) than at 22 °C. Accordingly, the developed scavenger has potential to be used during cold chain management for maintaining the postharvest quality of C_2H_4-sensitive produce. Adsorption experiments involving spectroscopy techniques (e.g. diffuse reflectance UV-Vis spectra, diffuse reflectance infrared Fourier transform spectroscopy and X-ray photoelectron spectroscopy) are persuaded to elucidate interactions among C_2H_4 molecules and the MMT surface, before and after $KMnO_4$ loading.



CHAPTER II

An Innovative Ethylene Scrubber Made of Potassium Permanganate Loaded on a Protonated Montmorillonite: A Case Study on Blueberries

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CHAPTER II. AN INNOVATIVE ETHYLENE SCRUBBER MADE OF POTASSIUM PERMANGANATE LOADED ON A PROTONATED MONTMORILLONITE: A CASE STUDY ON BLUEBERRIES

II.1 Introduction

The worldwide blueberries production grew by 78.4 % during the period from 2008 to 2016. Consequently, blueberries became the second soft fruit in 2017 showing the best economic benefits (FAO, 2017). The wide health-promoting properties and valued organoleptic characteristics of blueberries are the main causes of such consumers' interest. Blueberries are very perishable due to several physiological, physical, and pathological processes during postharvest life. Decay of blueberries (mainly due to *Botrytis cinerea*) and weight loss (mainly due to moisture loss) reduce the quality, and consequently, their shelf–life due to softening and skin wrinkling (Chiabrando & Giacalone, 2011; Perkins-Veazie, 2016). Therefore, appropriate postharvest techniques are needed to extend the blueberries shelf–life.

Low–temperature storage is widely used as a postharvest technique to maintain the quality of fruit and vegetables, especially blueberries (Kader, 2002; Paniagua et al., 2014). Blueberries are recommended to be stored at temperatures of 0 to 2 ºC (90–95 % RH) (Nunes et al., 2009; Perkins-Veazie, 2016). Freezing damages start to appear in blueberries below -1.5 ºC (Boyette et al., 1993). Then, a storage temperature of 2 ºC may be preferred to avoid freezing damages of blueberries during temperature fluctuations that occur in cold rooms. On the other side, such low storage temperatures are not maintained during retails periods. In fact, a wide variation has been reported to occur on the retail displays, with ranges of -1.2–19.2 ºC (refrigerated displays) and 7.6–27.7 ºC (non–refrigerated displays) (Nunes et al., 2009). Nevertheless, Ballinger et al. (1978) reported that blueberries for the fresh market should not be exposed to temperatures exceeding 10 ºC.

Fruit and vegetable storage at high CO_2 and low O_2 concentrations may extend the produce shelf–life using either MAP or controlled atmospheres (Kader, 2002). Particularly, CO_2 and O_2 concentrations of 4.4–10.6 and 0.9–2.2 mmol L^{-1}, respectively, controlled the decay incidence in MAP blueberries (Terry et al., 2009). Blueberries have low C_2H_4—considered the ripening hormone— production rates (0.8–8.1 pmol kg^{-1} s^{-1} at 5 ºC) (Crisosto et al., 1998b). Nevertheless, such trace C_2H_4 concentrations are physiologically active triggering ripening processes. In fact, weight and sugar content changes occurring during blueberries storage may be minimised by C_2H_4 removal (Chiabrando & Giacalone, 2011). Fungal germination and hyphal growth are also promoted in blueberries due to the C_2H_4 presence

(Zhu et al., 2012). Then, C_2H_4 removal may delay blueberries senescence with the subsequent economic impact. Additionally, the reduction of C_2H_4 concentration from the atmosphere surrounding fresh horticultural produce may reduce the refrigeration needs (Wills & Golding, 2015), leading to important energy savings.

$KMnO_4$ is a powerful agent that oxidizes C_2H_4 into CO_2 and H_2O (Wills & Golding, 2015). Accordingly, $KMnO_4$–based C_2H_4 scrubbers are the most common C_2H_4 removal systems during transport, distribution, and retail of produce (Martínez-Romero et al., 2007). Wang et al. (2018) reported that $KMnO_4$–based C_2H_4 scrubbers delayed weight loss and softening, while prevented decay and total phenolic content loss, in MAP blueberries. The use of nanoscaled support materials, such as MMT, or the reduction of their particle size (i.e. protonation), may enhance the ERR of $KMnO_4$–based scrubbers (Spricigo et al., 2017).

The present work aimed to study the effects of an innovative $KMnO_4$–based C_2H_4 scrubber, consisting of a protonated MMT, on the quality of MAP blueberries stored at 2 and 10 ºC. The effects of the developed C_2H_4 scrubber were compared with those of a commercial one. The effects of storage under air and MAP conditions without any C_2H_4 scrubber were also evaluated on the fruit quality. To the best of our knowledge, no other studies have been addressed on the effects of a C_2H_4 scavenger consisting of a protonated MMT loaded with $KMnO_4$ on the postharvest quality of blueberries.

II.2 Material and methods

II.2.1 Plant and chemical materials

Northern highbush blueberries (*Vaccinium corymbosum* var. Duke) were grown in the North of Spain (Salas, Asturias) according to biological and cultural management in an open-air cultivation parcel from the company 'Arándanos La Peña' (Asturias, Spain). Fully ripened blue stage fruit was hand-harvested in June 2017 during early morning and then cold–transported by car to the Universidad Politécnica de Cartagena. Blueberries were then stored at 2 ºC (90–95 % RH) until the next day when the experiment was conducted.

The mineral nanoclay Na^+–MMT (Cloisite® Na^+; cation–exchange capacity of 92 cmol(+) kg^{-1}) was obtained from Southern Clay Products Inc. (Gonzales TX, USA). HCl (36–38 %) and $KMnO_4$ were obtained from Sigma–Aldrich (Germany). A commercial $KMnO_4$–based C_2H_4 scrubber (Bi–On® R12; 55 × 55 mm sachets; 4.26 g (pellet form) per sachet; C_2H_4 removal capacity: 4.5 ± 0.5 L kg^{-1}) was obtained from Bioconservacion S.A. (Barcelona, Spain).

II.2.2 Preparation of potassium permanganate-modified montmorillonite material

A novel C_2H_4 scavenger based on $KMnO_4$, with MMT as support material, was prepared according to the procedure described by Avalos et al. (2008) with some modifications. Briefly, Na^+–MMT clay was dispersed in hot (60 ºC) distilled H_2O. The Na^+–MMT suspension was kept overnight at 30 ºC under continuous stirring. Then, the MMT was protonated by the addition of 0.025 M HCl (1 L per 100 g of clay) solution into the suspension, which was previously heated at 80 ºC, and it was stirred for 2 h at 80 ºC. After stirring, the protonated MMT suspension was centrifuged and washed several times with hot distilled H_2O until the elimination of chloride ions, which was indicated by a pH≈7. The final precipitate was then washed with absolute ethanol and dried overnight at 60 ºC in a forced–convection oven. The dry protonated clay was dispersed into hot H_2O and modified with 10 % (*w/w*) $KMnO_4$ dissolved in H_2O. The $KMnO_4$–modified clay suspension was stirred overnight at 30 ºC. Subsequently, the suspension was dried at 60 ºC to obtain the final $KMnO_4$–based protonated MMT (PMMT). The $KMnO_4$ concentration from the PMMT was determined with a UV–Vis spectrophotometer (Jasco V–630, Tokyo, Japan) according to Wills & Warton (2004).

The C_2H_4 uptake capacity of the obtained PMMT was 10.5 L kg^{-1} at 22 ºC, which was determined based on the procedure described by de Chiara et al. (2015). Tyvek® (Dupont, Wilmington DE, USA) sachets (55 × 55 mm) were prepared; containing each sachet 0.7 g of PMMT. The PMMT quantity per sachet was selected to remove the same C_2H_4 amount as the Bi–On® R12 sachets. The commercial C_2H_4 scrubber was also characterized by WDXRF spectrometry (using a Bruker AXS S4 Pioneer XRF Spectrometer, Billerica MA, USA) showing an elemental constitution typical of a zeolite.

II.2.3 Modified atmosphere packaging of samples with the potassium permanganate–based sachets

Blueberries without defects and with similar size were selected for the experiment. Blueberries were processed in a disinfected cold room at 8 ºC. Blueberries (120.7 ± 0.6 g) were placed in 0.25–L rigid PP trays being then heat-sealed on the top with a BOPP film (35 µm thickness; Plásticos del Segura, Murcia, Spain) to achieve a passive MAP. The measured O_2 and CO_2 permeabilities of the BOPP film were 174,213- and 175,341-mL m^{-2} $days^{-1}$ atm^{-1}, respectively, at 10 ºC and 0 % RH (Lyssy manometric gas permeability tester L100–5000; Systech Instruments Ltd, UK). One C_2H_4 scrubber sachet, either the commercial or the developed one, was placed in the centre of each tray on the inner side of the film with a double-sided tape. Blueberry samples (without scrubber) were also

packaged under air conditions in vented PP clams as usually done at the retail level. Abbreviations (AIR, MAP, MAP+COM_{BION} and MAP+PMMT) of blueberry treatments (atmosphere/scavenger) are described in Table II.1. Samples were stored in darkness at 2 and 10 ºC up to 46 days. The 2 ºC storage temperature was selected from the recommended 0–2 ºC range (Nunes et al., 2009; Perkins-Veazie, 2016) to avoid freezing damages of blueberries due to fluctuations that occur in cold rooms. The 10 ºC storage temperature was selected as the maximum storage temperature recommended for blueberries during a retail period (Ballinger et al., 1978). The 46–days storage time was chosen based on decay incidence in preliminary experiments. The gas composition within MAP packages and quality parameters of samples were analysed at the following sampling times: 0 (processing day) 7, 14, 21 and 46 days. A total of 200 samples (5 replicates × 4 treatments × 2 storage temperatures × 5 sampling times) were prepared for the experiment.

Table II.1. Description of treatments (source: Own elaboration).

Treatment	Packaging atmosphere	C_2H_4 scrubber
AIR	Air	None
MAP	MAP	None
MAP+COM_{BION}	MAP	Commercial scrubber: Bion R-12 (4 g/sachet)
MAP+PMMT	MAP	$KMnO_4$ on protonated MMT (0.7 g/sachet)

MAP: modified atmosphere packaging; MMT: montmorillonite

II.2.4 Respiration and ethylene production rates

The RR and C_2H_4 production rate of blueberries were daily determined at 2 and 10 ºC for 11 days using a closed system as previously described (Martínez-Hernández et al., 2011). Blueberries (120.8 ± 0.7 g) with uniform in size and free from defects were randomly selected and placed into 0.75–L glass jars. The prepared jars with the blueberries were left overnight at 2 or 10 ºC to ensure fruit equilibration to these temperatures. Five replicates (5 jars) per storage temperature were prepared. Jars were vented with a continuous flow (20 mL min^{-1}) of humidified air to avoid CO_2 accumulation higher than 0.13 mmol L^{-1} inside the jars (Watada, 1986), which may lead to altered metabolic respiration processes. On each measurement day, the jars were set to a closed system, to accumulate produced CO_2, for 3 h prior to gas sampling. Gas sampling (1 mL) was done from the headspace of jars using a gas-tight syringe and then injected into the GC instrument.

The GC conditions for CO_2 determination were: oven, injector and TCD temperatures of 80, 120 and 200 ºC, respectively. Air and H_2 were used as gas carriers at 30 and 2 mL min^{-1},

respectively. A stainless–steel column packed with Hayesep Q (1/8”, 80/100 mesh size; Teknokroma, Barcelona, Spain) followed by a stainless–steel column packed with molecular sieve 5A (1/8”, 80/100 mesh size; Teknokroma, Barcelona, Spain) were used for CO_2/O_2 determination.

For C_2H_4 measurements, the oven, injector and flame ionization detector (FID) temperatures were 80, 120 and 250 ºC, respectively. Air and H_2 were used as gas carriers at 350 and 35 mL min^{-1}, respectively. A stainless–steel column packed with Porapak Q (1/8”, 80/100 mesh size; Teknokroma, Barcelona, Spain) was used for C_2H_4 determination.

Gas calibration was done by comparison with an external CO_2 /O_2 /C_2H_4 mixture (gas molar fraction 10 % / 10 % /10 ppm) standard (Praxair, Molina de Segura, Spain). Five measurements per jar were daily performed for up to 9 days.

II.2.5 Gas composition within the modified atmosphere packages

For in-packages gas composition measurements, an adhesive septum was stuck on the BOPP film surface of the blueberry packages and headspace gas samples (1 mL) were withdrawn from the package headspace. Gas samples were injected into the corresponding injection port of a GC instrument (7820A GC System, Agilent Technologies, Santa Clara CA, USA), and then measured following the corresponding above–described GC configuration. The GC conditions and the injection port for CO_2 measurements are the same for O_2 measurements. Five measurements per tray were made every sampling day

II.2.6 Weight loss

Weight loss was calculated as the percentage difference between the initial and final weight of the experimental units. An analytical balance (Ohaus EX124; Parsippany, New Jersey, USA) was used.

II.2.7 Skin morphology

The surface microstructure of blueberry skin of samples was monitored at 2 and 10 ºC at every sampling time (0, 7, 14, 21 and 46 days). Individual blueberries were randomly selected from each treatment after opening the packages. Skin samples of 1 cm^2 were cut from the blueberry units and then dehydrated using an acetone series (30, 50, 20, 90 and 100 % (v/v) acetone solutions) and a critical point dryer (CPD 030, BAL–TEC AG, Balzers, Liechtenstein). Subsequently, the dried samples were adhered to on aluminium discs with a double-sided carbon tape and then sputter-coated with gold (SC7610, Quorom Technologies, East Sussex, UK). The prepared samples were observed by SEM (using a

Hitachi S–3500N instrument; Tokyo, Japan) operated at an accelerating voltage of 15 kV and a working distance of 15 mm. Images were acquired by using the S-3500N Scanning Electron Microscope 50E-5121 software (v. 10-12-2254/10-03; Hitachi High-Technologies Corp., Tokyo, Japan).

Scrubber material contamination to blueberry fruit was assessed by elemental analysis of the SEM–prepared dried blueberry skin samples. The assay was carried out using an energy–dispersive X-ray analyser (Flash 5010, Bruker AXS Microanalysis, Berlin, Germany) coupled to the SEM instrument.

II.2.8 Firmness

Fruit firmness was evaluated on 45 randomly selected berries per treatment at each sampling time (0, 7, 14, 21 and 46 days). Once packages were opened, samples were allowed to equilibrate to room temperature for 1 h prior to firmness measurements. A compression test was carried out using a texture analyser (CT3TM; Brookfield Ametek, Middleboro, MA, USA) equipped with a 4.5–kg load cell, and a 2–mm diameter cylinder stainless probe. Each blueberry was compressed 5 mm on the equatorial region using a test speed of 1 mm s^{-1} and a trigger force of 0.5 g following the procedures described by Chen et al. (2015) and Paniagua et al. (2014). The peak force (N) necessary to achieve the target distance was recorded.

II.2.9 Physicochemical quality

II.2.9.1 Soluble solids content

The SSC was analysed from the blueberries juice. This juice was extracted from 10 berries (randomly selected) using a mortar followed by filtration through a four−layers cheesecloth. The SSC was determined using a digital hand−held refractometer (Atago N1; Tokyo, Kanto, Japan) at 20 ºC and expressed as % (sugar equivalents in g 100 g^{-1}).

II.2.9.2 pH and titratable acidity

A pH−meter (Basic20, Crison; Alella, Cataluña, Spain) was used to measure the pH of the blueberry juice. TA was determined by titrating (T50 titrator; Metter Toledo; Milan, Italy) a diluted juice (5 mL juice +45 mL distilled H_2O) with 0.1 M NaOH to an endpoint of pH 8.1. TA was expressed as citric acid in g L^{-1}. The MI of blueberries was determined from the SSC/TA ratio.

II.2.9.3 Skin colour

Blueberry skin colour was individually determined from at least 18 berries (randomly selected) per tray using a colourimeter (Chroma Meter CM–A131, Minolta; Tokyo, Kanto, Japan) with a 2 º–observer angle and an 8–mm viewing aperture. The colourimeter used the CIE standard illuminant D65 that represents daylight more completely and accurately than B and C illuminants (Pathare et al., 2013). Measurements were obtained using the CIE *L*, a** and *b** tristimulus values, which provide more uniform colour differences concerning human perception compared to Hunter L a b (Pathare et al., 2013). Before measurements, the colourimeter was calibrated with a white reference plate (illuminant D65). The waxy bloom on the blueberry surface was previously removed with a towel paper to avoid heterogeneous colour measurements. Three colour readings were taken on the equatorial axis of each berry at three equidistant points. The three measurement values were automatically averaged by the device. Total colour differences (ΔE*) index represents the distance vector modulus between the initial colour values and the actual colour coordinates. The colour index ΔE* was used in this experiment to better describe the changes of all three CIELab parameters (*L*, a*, b**). The ΔE* index was calculated throughout storage, compared to their respective initial values, as previously described (Rhim et al., 1989).

II.2.10 Decay incidence and microbiological analyses

Fungal decay incidence was visually estimated on each individual fruit and decayed berries were expressed as a percentage of the total berries (Almenar et al., 2010). Any blueberry with visible mycelial fungal growth was considered as decayed fruit.

Standard enumeration methods were used to determine the growth of mesophiles, psychrophiles, *Enterobacteriaceae* and Y+M of samples according to Castillejo et al. (2016). Briefly, 10−fold dilution series were prepared in 9 mL of sterile peptone saline solution. Mesophiles, psychrophiles and *Enterobacteriaceae* were pour-plated, while Y+M were spread–plated. The following media/incubation conditions were used: plate count modified agar for mesophilic and psychrophilic counts with incubations of 30 ºC/48 h and 5 ºC/7 days, respectively; violet red bile dextrose agar for *Enterobacteriaceae* with an incubation of 37 ºC/48 h; and rose Bengal agar for Y+M with an incubation of 25 ºC/3–5 days. All microbial counts were reported as log colony forming units per g of product (log CFU g^{-1}). Each of the five replicates was analysed in duplicate.

II.2.11 Sensory evaluation

Sensory analyses were performed according to international standards (ASTM, 1986). Sensory tests were conducted in a standard room (ISO_8586:2012; ISO (2012)) equipped

with 10 individual tasting booths. Berries were randomly selected and served at room temperature in white plastic glasses coded with three random digit numbers. Still mineral H_2O was used as a palate cleanser. The panel consisted of 10 assessors (5 women/5 men, aged 22–70 years) screened by their sensory ability (visual appearance, colour, aroma, flavour and texture). A 9−points rating scale of damage incidence and severity was scored for off−colours, off−flavours and off−odours (9: none; 7: slight; 5: moderate, LU; 3: strong; 1: severe). Visual appearance, aroma, flavour, texture and overall quality were assessed using a 9−points hedonic scale of acceptability (9: extremely good; 7: moderately good; 5: fair, LU; 3: moderately bad; 1: extremely bad).

II.2.12 Statistical analysis

The experiment was conducted in a three−factor (treatment for ethylene control × storage temperature × storage time) design and subjected to ANOVA using SPSS software (v.19 IBM, New York, USA). Statistical significance was assessed at $P \leq 0.05$, and Tukey's multiple range test was used to separate the means.

II.3 Results and discussion

II.3.1 Respiration and ethylene production rates

II.3.1.1 Respiration rate

Storage temperatures significantly ($P \leq 0.001$) affected the RR of samples. Furthermore, the storage temperature × time was significant ($P \leq 0.001$) for the RR of samples (Figure II.1a). Blueberries showed an initial RR of 87.2 ± 15.5 and 50.7 ± 8.0 nmol kg^{-1} s^{-1} at 2 and 10 ºC, respectively, on day 1 (Figure II.1a). To further elucidate the observed higher initial RR at 2 ºC compared with 10 ºC, RR was also determined at intermediate temperatures of 5 and 7 ºC (Figure II.2). Initial RR of samples at 5 and 7 ºC were in the same range of the RR of 10 ºC–samples with values of 46.4 ± 4.2 and 49.4 ± 14.9 nmol kg^{-1} s^{-1} CO_2, respectively. Blueberries RR at low temperatures has been reported at 0 ºC and > 5 ºC (Beaudry et al., 1992) but not at 2 ºC.

The high initial RR at 2 ºC, compared with 10 ºC, could be attributed to the abiotic stress response of the fruit to such low storage temperature that is enough for the respiration–related enzymes to start to show activity, contrary to 0 ºC, which is even enhanced due to chilling stress. Such initial higher RR in low storage temperature ranges (just above 0 ºC) —and related physiological changes associated to ripening— compared with storage at 0

ºC has been also reported in other fruit and vegetables (Barbosa et al., 2011; Crisosto et al., 1999).

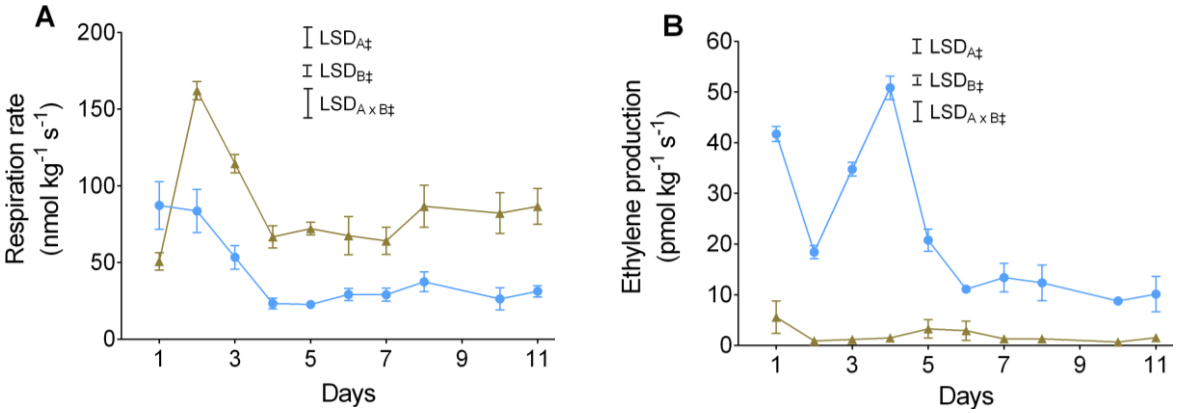


Figure II.1. Respiration (a) and ethylene production (a) rates of blueberry fruit at 2 (●) and 10 (▲) ºC (mean (n=5)±standard deviation). The uppercase letters (subscripts) A and B denote time and temperature, respectively. ‡ significance for $P \leq 0.001$. LSD: Least significant difference (source: Own elaboration).

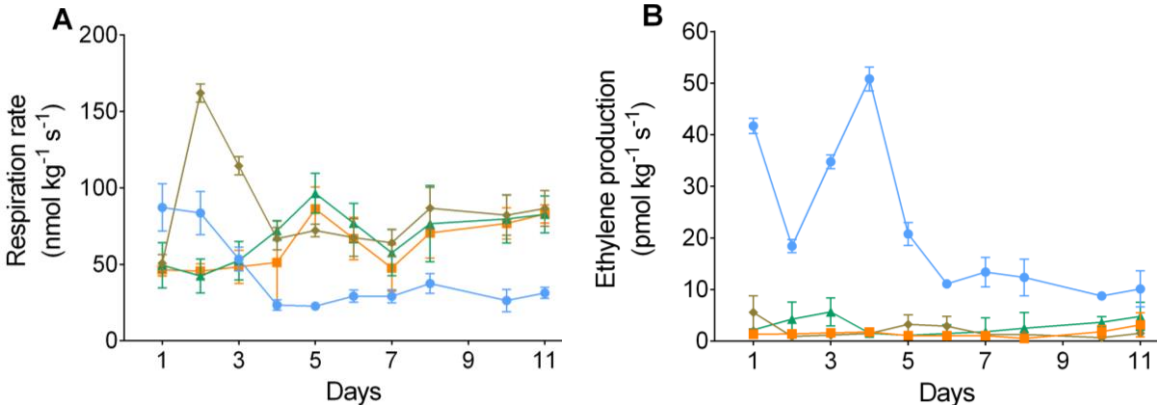


Figure II.2. Respiration (a) and ethylene production (b) rates of blueberry fruit at 2 (●), 5 (■), 7 (▲) and 10 (◆) ºC (mean (n=5)±standard deviation) (source: Own elaboration).

Particularly, the hypothetical abiotic stress response on the initial RR was also observed in carrots with higher initial RR at 5 ºC compared with 10 ºC that were downregulated to the opposite behaviour (RR at 10 ºC higher than 5 ºC) from 40 h until the end of storage (Barbosa et al., 2011). Nevertheless, these initial specific responses, limited to the mentioned temperature ranges, were not observed when storing the fruit at a lower temperature of 0 ºC (Crisosto et al., 1999). The latter finding may be explained due to the low temperature–inhibition of these enzymatic systems.

According to the observed chilling damages observed by Crisosto et al. (1999) in peaches, blueberries flesh showed translucency —a typical chilling injury symptom of some chilling sensitive produce— after 46 days at 2 ºC (Figure II.3). A similar flesh translucency has been

also observed in tomatoes stored at low storage temperatures (Sharom et al., 1994). Nevertheless, the translucency is not appreciated by consumers in small fruit that is whole eaten as a single bite, like blueberries, contrary to bigger fruit that need to be cut in several pieces prior to consumption.

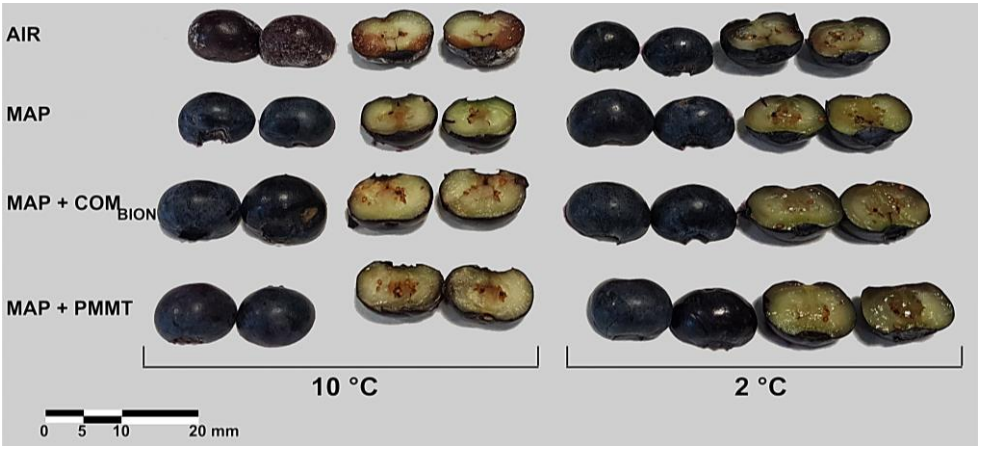


Figure II.3. Blueberry fruit stored under different packaging conditions at 2 and 10 ºC on day 46 (source: Own elaboration).

The initial chilling stress–enhanced RR of blueberries at 2 ºC was downregulated during storage showing a stabilized RR (29.0–37.4 nmol kg^{-1} s^{-1}) from day 5 until the end of the RR experiment (Figure II.1a). Samples stored at 10 ºC showed an RR increment on day 3 that was also downregulated from days 4–5 until the end of the RR experiment with a stabilized RR of 64.1–86.7 nmol kg^{-1} s^{-1} (Figure II.1a). The latter RR increase at 10 ºC was also observed at 5 and 7 ºC although such RR maximum peak was delayed from day 3 (as observed at 10 ºC) to day 6 (Figure II.2).

II.3.1.2 Ethylene production rate

As similarly observe for RR, storage temperatures significantly ($P \leq 0.001$) affected the C_2H_4 production rate of samples and a storage temperature × time ($P \leq 0.001$) interaction effect was also observed (Figure II.1b). Like RR, blueberries stored at 2 ºC showed the highest initial C_2H_4 production rate (41.7 ± 1.5 pmol kg^{-1} s^{-1}) on day 1 (Figure II.1b). The C_2H_4 production rates at 5 and 7 ºC were also determined (Figure II.2) showing the same behaviour as RR. The observed initial C_2H_4 production rate at 2 ºC declined to 18.4 ± 1.3 pmol kg^{-1} s^{-1} after 2 days and then increased up to 50.8 ± 2.3 pmol kg^{-1} s^{-1} after 4 days. The previous finding may be explained by the related abiotic stress at such low temperature, being subsequently downregulated when the plant cells metabolism was adapted to that temperature. The high initial C_2H_4 production rate at 2 ºC decreased during storage, corroborated a kind of transient stress like chilling stress. Although the reported blueberry C_2H_4 production rates are typically low (compiled by Kader (2002)), it is crucial to remove

the in–package C_2H_4 since trace C_2H_4 concentrations are enough to stimulate fungal decay (Perkins-Veazie, 2016). A shelf-life of 35 to 40 days has been reported for blueberries stored under controlled atmospheres (0.7–0.9 mmol L^{-1} O_2 and 5.3–8.9 mmol L^{-1} CO_2) at -0.5–0 ºC (Frisina et al., 1988; Hruschka & Kushman, 1963). Such shelf–life could be even overpassed with the use of C_2H_4 removal methods like $KMnO_4$–based scrubbers although it has not been still issued to the best of our knowledge. Furthermore, the C_2H_4 removal may minimise the refrigeration needs of produce as proposed by Wills & Golding (2015), avoiding the observed chilling stress responses on RR and C_2H_4 production rates of blueberries, without forgetting the important energy savings.

II.3.2 Gas composition within the modified atmosphere packages

II.3.2.1 Carbon dioxide and oxygen

A significant ($P \leq 0.01$) treatment × time interaction was observed for CO_2 and O_2 concentrations at 2 ºC; while this interaction was only significant ($P \leq 0.001$) at 10 ºC for O_2 data, but no for CO_2 data ($P > 0.05$). Significant ($P \leq 0.001$) differences in CO_2 data were observed between treatments at both storage temperatures. The MAP steady–state of samples was reached after approximately 20 days at 2 ºC (0.8 ± 0.1 mmol L^{-1} O_2/5.8 ± 0.4 mmol L^{-1} CO_2) and 14 days at 10 ºC (0.7 ± 0.1 mmol L^{-1} O_2/6.8 ± 0.7 mmol L^{-1} CO_2) (Figure II.4a, b). The reported minimum critical O_2 partial pressures —where respiration quote ($RRCO_2/RRO_2$) breakpoint occurs leading to harmful effects from anaerobic conditions inside packaging— for blueberries are 0.8 mmol L^{-1} at 0–5 ºC and 0.9 mmol L^{-1} at 10 ºC (Beaudry et al., 1992). The maximum CO_2 concentration tolerated by blueberries is 9.8 mmol L^{-1} (Cameron et al., 1994). The O_2 concentration during the 46 days–storage, at both storage temperatures, was above the critical O_2 concentrations for blueberries. Furthermore, CO_2 concentrations during the 46 days–storage at 2 ºC were also above the critical CO_2 concentrations for blueberries. Nevertheless, the safe CO_2 concentrations were overpassed on day 33 at 10 ºC (Figure II.5).

Samples stored with the commercial sachets (MAP+COM_{BION}) showed the lowest CO_2 partial pressures during the first 20 days of storage (Figure II.4a, b). The latter finding may be explained since zeolites (support material of the COM_{BION} scrubber) has higher CO_2 adsorption proficiency than MMT (support material of the PMMT scrubber) (Kadoura et al., 2016). Consequently, the hereby developed C_2H_4 scrubber is preferred compared to the commercial one since it does not interfere with the desired CO_2 accumulation in MAP.

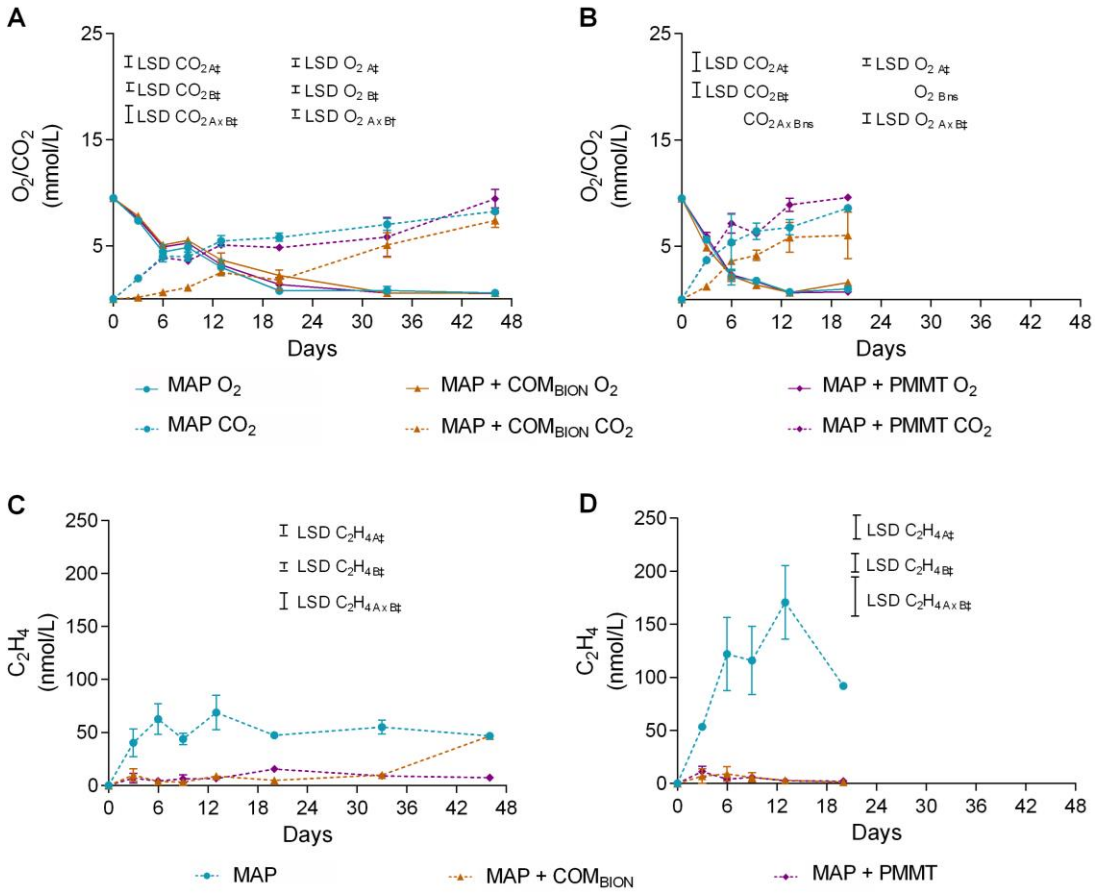


Figure II.4. Gas partial pressures (O_2/CO_2; a, b; C_2H_4: c, d) inside blueberry packaging during storage at 2 ºC (a, c) and 10 ºC (b, d) for 21 and 46 days, respectively, using different C_2H_4 scrubber conditions (see Table II.1) (mean (n=5)±standard deviation. The uppercase letters (subscripts) A and B denote time and treatment, respectively. † and ‡ significance for $P \leq 0.01$ and 0.001, respectively. LSD: Least significant difference (source: Own elaboration).

II.3.2.2 Ethylene

A significant ($P \leq 0.001$) interaction treatment × time on C_2H_4 partial pressures at both 2 and 10 ºC was observed. The CO_2 and C_2H_4 partial pressures were significantly ($P \leq 0.001$) affected during storage at both temperatures by incorporating C_2H_4 scrubbers. The C_2H_4 concentrations at both storage temperatures were decreased ($P \leq 0.001$) when the C_2H_4 scrubber sachets were used (Figure II.4c, d). An average C_2H_4 concentration of 52.2 ± 8.6 nmol L^{-1} was observed throughout storage at 2 ºC (Figure II.4c). Meanwhile, a maximum C_2H_4 concentration of 170.7 ± 34.8 nmol L^{-1} was observed at 10 ºC after 10 days, followed by a progressive reduction reaching similar low C_2H_4 concentrations like those of samples stored at 2 ºC for 46 days (Figure II.5).

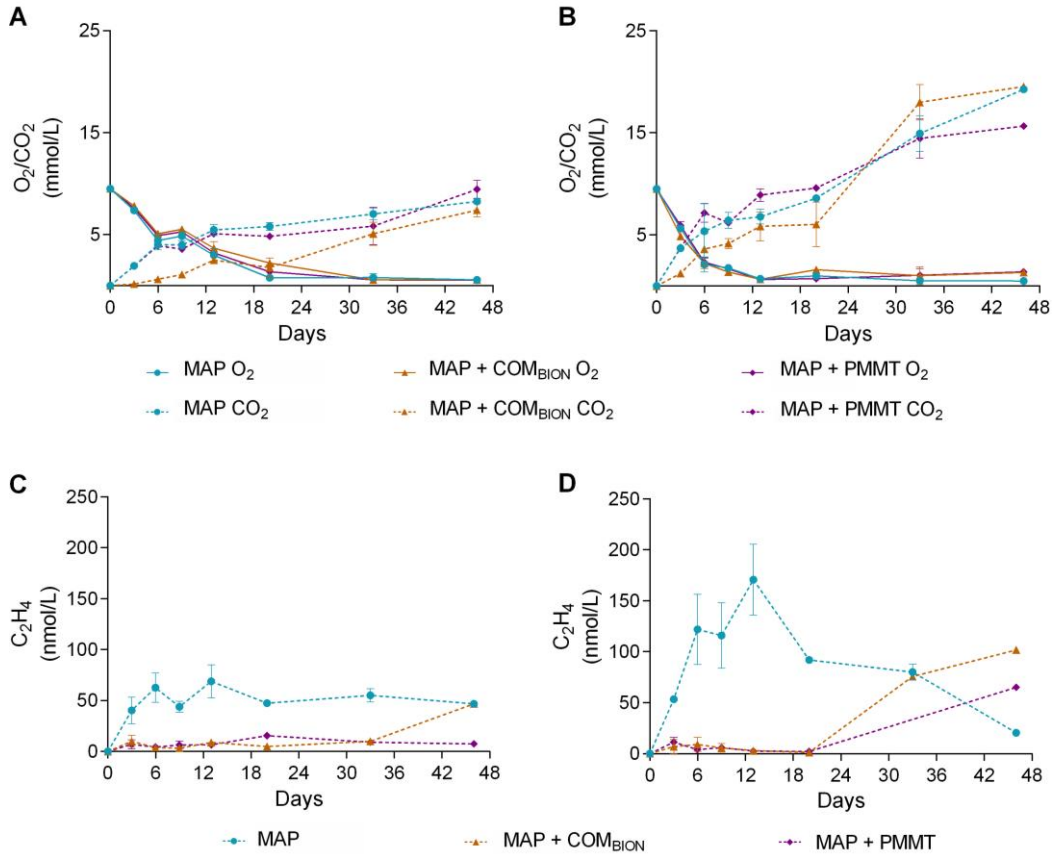


Figure II.5. Gas partial pressures (O_2/CO_2; a, b; C_2H_4: c, d) inside blueberry packaging during storage at 2 ºC (a, c) and 10 ºC (b, d) up to 46 days using different C_2H_4 scrubber conditions (see Table II.1) (mean (n=5)±standard deviation) (source: Own elaboration).

The C_2H_4 concentrations of MAP+COM_{BION} and MAP+PMMT samples were 1.4 ± 0.3 and 2.1 ± 0.8 nmol L^{-1}, respectively, after 20 days at 10 ºC followed by a pronounced increase reaching concentrations of 101.8 ± 0.0 and 65.0 ± 0.0 nmol L^{-1}, respectively, after 46 days (Figure II.5). The MAP+COM_{BION} and MAP+PMMT samples showed C_2H_4 concentrations below 10 nmol L^{-1} during 33 days at 2 ºC. The latter data indicate a better $KMnO_4$ retention at 2 ºC as observed in Figure II.6. The higher C_2H_4 concentrations observed in MAP samples for 14 days at 10 ºC may be owed to a metabolic response to the high CO_2/low O_2 partial pressures reached by MAP at such temperature (as previously commented). The latter findings can be attributed to the low C_2H_4 partial pressures reached under MAP conditions at 2 ºC compared with the C_2H_4 partial pressures reached under the same packaging conditions at 10 ºC (Figure II.4c, d).

Conclusively, the developed C_2H_4 scrubber showed a higher C_2H_4 removal capacity than the commercial one with a lower material quantity needed (0.70 g per sachet). Furthermore, the commercial C_2H_4 scrubber showed some CO_2 adsorption which is undesirable during MAP.

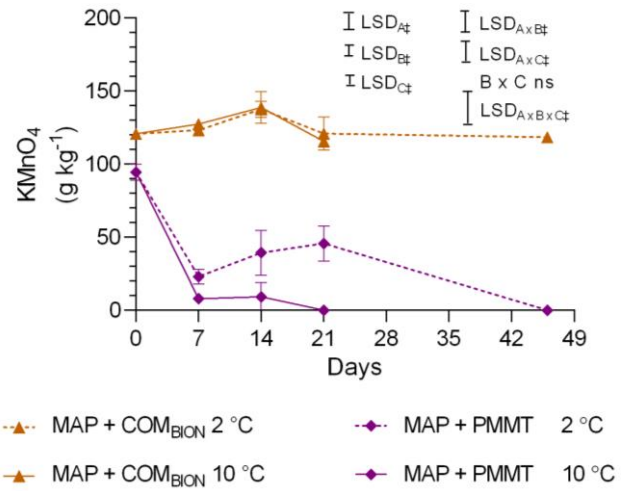


Figure II.6. Potassium permanganate ($KMnO_4$) concentration in ethylene scrubber sachets during storage of blueberries at 2 and 10 ºC for 21 and 46 days, respectively, using different C_2H_4 scrubber conditions (see Table II.1) (mean (n=5)±standard deviation). The uppercase letters (subscripts) A, B and C denote time, temperature, and treatment, respectively. ns and ‡ significance for *P* ≤ not significant and 0.001, respectively. LSD: Least significant difference (source: Own elaboration).

II.3.3 Changes in the $KMnO_4$ content of scrubber materials during blueberries storage

The $KMnO_4$ content showed a significant ($P \leq 0.001$) temperature × time interaction, but not for temperature × treatment. Nevertheless, the treatment × temperature × time interaction was significant ($P \leq 0.001$) for the $KMnO_4$ content. The remaining $KMnO_4$ contents in the COM_{BION} and PMMT sachets used in MAP blueberries were 115.6 ± 0.0 and 0.0 ± 0.1 g kg^{-1}, respectively, after 21 days at 10 ºC (Figure II.6). The $KMnO_4$ content of PMMT sachets was decreased after 7 days, while COM_{BION} sachets showed minimum $KMnO_4$ changes during blueberry storage, regardless of the storage temperature (Figure II.6). The latter finding is explained by a higher oxidative reactivity of the PMMT scrubber compared with the COM_{BION} scrubber since the chemical reactivity/selectivity of $KMnO_4$ can be improved using support materials of smaller particle size (Spricigo et al., 2017). In that sense, Spricigo et al., (2017) observed that $KMnO_4$–loaded nanoscaled materials can remove C_2H_4 more efficiently than microscaled materials, which can be explained by the large surface area that nanoparticles possess.

The PMMT scrubber showed a higher C_2H_4 removal efficiency than the COM_{BION} scrubber since 6.1–fold lower PMMT scrubber quantity was needed to obtain the same C_2H_4 partial pressures reductions as COM_{BION}. Conclusively, the methodology used to reduce the MMT particle size in the PMMT scrubber is justified by the similar C_2H_4 removal efficiency compared to the commercial scrubber using less scrubber quantity.

II.3.4 Weight loss

The weight loss of blueberries stored under MAP conditions, independently of the C_2H_4 scrubber presence, was controlled ($P \leq 0.001$) during storage either at 2 or 10 ºC (Table II.2). No significant ($P > 0.05$) treatment × temperature × time interaction was observed on the weight loss of samples (Table II.2). Weight losses of 1.4 ± 0.1 and 2.4 ± 0.3 % were registered in AIR samples after 21 days at 2 and 10 ºC, respectively. Similar to our results, a weight loss of 1 % has been reported in blueberries stored in vented cups after 21 days at 1 ºC (W. R. Miller et al., 1993). Nevertheless, AIR samples reached a weight loss of 8.5 ± 1.8 % after 46 days at 2 ºC (Table II.2). The latter weight loss is unacceptable since weight losses higher than 5 % would lead to a non–marketable product (Almenar et al., 2008) due to a freshness reduction caused by the firmness loss. The temperature effect on the weight loss was less important than the effect of the atmospheric composition (Table II.2), as previously reported in blueberries stored at 3 or 10 ºC (Almenar et al., 2010). The weight loss during fruit storage is mainly due to the H_2O loss, which is aggravated due to configuration changes of plant cells during senescence. The MAP use in blueberries is then justified, as also previously recommended (Chiabrando & Giacalone, 2011), due to the observed minimum weight losses compared to ventilated samples (AIR).

Table II.2. Decay, weight loss, firmness, total soluble solids content and titratable acidity of packaged (modified atmosphere packaging; MAP) blueberry fruit using a commercial C_2H_4 scrubber (COM_{BION}) and protonated montmorillonite (PMMT) during storage at 2 and 10 ºC for 21 and 46 days, respectively (mean (n=5)±standard deviation) (source: Own elaboration).

Storage Time	Temperature	Treatment	Weight loss (%)	Firmness (N)	SSC (%)	TA (citric acid, g L^{-1})	MI (SSC/TA)	Decay (%)
Processing day			-	1.96 ± 0.1	9.8 ± 0.1	7.5 ± 0.6	13.0 ± 1.0	0.0 ± 0.0
Day 7	2 ºC	AIR	0.5 ± 0.1	1.91 ± 0.03	10.2 ± 0.1	7.3 ± 0.3	14.0 ± 0.4	3.3 ± 0.5
		MAP	0.0 ± 0.2	2.06 ± 0.15	10.9 ± 0.8	7.8 ± 0.8	14.1 ± 0.8	2.3 ± 0.4
		MAP+COM_{BION}	0.0 ± 0.0	2.03 ± 0.07	9.7 ± 0.2	6.2 ± 0.3	15.7 ± 1.0	0.9 ± 0.0
		MAP+PMMT	0.0 ± 0.9	2.03 ± 0.12	10.7 ± 0.3	7.5 ± 0.3	14.4 ± 0.7	1.1 ± 0.0
	10 ºC	AIR	0.8 ± 0.3	1.80 ± 0.11	10.5 ± 0.4	5.5 ± 0.3	19.3 ± 1.7	7.9 ± 0.3
		MAP	0.1 ± 0.1	1.90 ± 0.12	10.4 ± 0.1	6.8 ± 0.2	15.3 ± 0.4	4.7 ± 0.4
		MAP+COM_{BION}	0.0 ± 0.0	1.88 ± 0.02	11.2 ± 0.4	6.7 ± 0.3	16.7 ± 1.0	1.0 ± 0.1
		MAP+PMMT	0.2 ± 0.4	1.98 ± 0.18	10.0 ± 0.8	6.7 ± 0.5	15.0 ± 0.7	4.1 ± 0.2
Day 14	2 ºC	AIR	0.9 ± 0.1	1.96 ± 0.04	9.9 ± 0.4	5.6 ± 0.4	17.6 ± 0.6	7.0 ± 1.3
		MAP	0.0 ± 0.3	1.96 ± 0.05	10.5 ± 0.8	7.9 ± 0.5	13.4 ± 1.8	3.9 ± 0.9
		MAP+COM_{BION}	0.0 ± 0.3	2.03 ± 0.04	10.0 ± 0.1	5.9 ± 0.2	16.9 ± 0.7	1.9 ± 0.0
		MAP+PMMT	0.0 ± 0.8	2.05 ± 0.08	10.5 ± 1.0	8.2 ± 0.2	12.8 ± 0.9	2.3 ± 0.5
	10 ºC	AIR	1.3 ± 0.4	1.60 ± 0.04	10.0 ± 0.3	5.4 ± 0.6	18.8 ± 1.9	21.7 ± 0.2
		MAP	0.0 ± 0.3	1.79 ± 0.07	10.4 ± 0.4	5.7 ± 0.1	18.2 ± 0.9	8.1 ± 0.9

Table II.2. Continued.

Storage Time	Temperature	Treatment	Weight loss (%)	Firmness (N)	SSC (%)	TA (citric acid, g L^{-1})	MI (SSC/TA)	Decay (%)
		MAP+COM_{BION}	0.0 ± 0.3	1.83 ± 0.04	9.5 ± 0.1	5.5 ± 0.6	17.4 ± 1.9	4.9 ± 0.7
		MAP+PMMT	0.0 ± 0.8	1.91 ± 0.12	10.5 ± 0.9	6.2 ± 0.5	16.9 ± 0.4	5.1 ± 1.8
Day 21	2 ºC	AIR	1.4 ± 0.1	2.03 ± 0.04	10.1 ± 0.4	6.5 ± 0.1	15.4 ± 0.4	11.8 ± 1.1
		MAP	0.0 ± 0.3	2.05 ± 0.01	10.9 ± 0.2	8.1 ± 0.3	13.4 ± 0.4	5.8 ± 1.8
		MAP+COM_{BION}	0.0 ± 0.2	1.95 ± 0.02	9.9 ± 0.2	7.1 ± 0.8	14.0 ± 1.7	1.9 ± 0.0
		MAP+PMMT	0.0 ± 0.9	2.04 ± 0.07	9.9 ± 0.4	9.0 ± 0.3	11.0 ± 0.8	2.8 ± 0.9
	10 ºC	AIR	2.4 ± 0.3	1.44 ± 0.03	10.1 ± 0.3	5.3 ± 0.4	19.0 ± 2.0	52.6 ± 0.5
		MAP	0.0 ± 0.2	1.72 ± 0.13	10.0 ± 0.0	6.7 ± 0.3	15.0 ± 0.7	9.1 ± 0.9
		MAP+COM_{BION}	0.0 ± 0.2	1.84 ± 0.09	10.3 ± 0.2	5.4 ± 0.2	19.0 ± 0.3	8.7 ± 0.8
		MAP+PMMT	0.0 ± 0.2	1.80 ± 0.01	9.6 ± 0.1	6.0 ± 0.0	16.1 ± 0.2	8.3 ± 2.7
Day 46	2 ºC	AIR	8.5 ± 1.8	2.08 ± 0.00	9.0 ± 0.0	7.0 ± 0.0	12.9 ± 0.0	17.8 ± 1.1
		MAP	0.0 ± 0.0	2.07 ± 0.00	11.0 ± 0.0	6.1 ± 0.0	18.1 ± 0.0	7.7 ± 1.8
		MAP+COM_{BION}	0.0 ± 0.3	2.04 ± 0.00	9.9 ± 0.0	7.1 ± 0.0	13.9 ± 0.0	4.9 ± 0.0
		MAP+PMMT	0.0 ± 0.8	1.98 ± 0.00	10.1 ± 0.0	6.7 ± 0.0	15.1 ± 0.0	3.7 ± 0.9
	10 ºC	AIR	—	—	—	—	—	—
		MAP	—	—	—	—	—	—

Table II.2. Continued.

Storage Time	Temperature	Treatment	Weight loss (%)	Firmness (N)	SSC (%)	TA (citric acid, g L^{-1})	MI (SSC/TA)	Decay (%)
		$MAP+COM_{BION}$	—	—	—	—	—	—
		MAP+PMMT	—	—	—	—	—	—
	Gas treatment (A)		(0.4)‡	(0.07)‡	(0.2)*	(0.4)‡	(1.0)‡	(0.8)‡
	Temperature (B)		(0.2)*	(0.05)‡	ns	(0.3)‡	(0.7)‡	(0.5)‡
	Time (C)		(0.4)‡	(0.08)‡	(0.4)‡	(0.5)‡	(1.1)‡	(0.8)‡
	A×B		ns	(0.08)†	(0.4)‡	(0.6)‡	ns	(1.1)‡
	A×C		(0.8)‡	ns	(0.5)*	(0.9)‡	(2.1)‡	(1.7)‡
	B×C		ns	(0.11)‡	ns	(0.6)‡	(1.5)‡	(1.2)‡
	A×B×C		ns	(0.13)*	(0.9)†	(1.3)‡	(3.0)‡	(2.4)‡

SSC: Total soluble solids content; TA: Titratable acidity; MI: Maturity index.
Values within parentheses represent the least significant difference.
ns, *, †, ‡ significance for $P \leq$ not significant, 0.05, 0.01, and 0.001, respectively.

II.3.5 Skin morphology

The SEM images (Figure II.7) revealed more pronounced wrinkles in MAP samples stored at 10 ºC for 21 days compared with samples stored at 2 ºC. Focussing on the best-preserved samples (those maintained at 2 ºC), skin cells of MAP blueberries with C_2H_4 scrubbers (Figure II.7b, c) were less dehydrated than those samples stored under air conditions (Figure II.7a). Epicuticular wax particles —responsible for the high skin resistance of blueberries to H_2O vapour and gas diffusion (Cameron et al., 1994)— that conform to the characteristic bloom on the blueberry surface (Cline, 1996) were also widely observed (Figure II.7). Therefore, although no differences in weight loss percentages of MAP samples were found between storage temperatures for 21 days, plant cell morphology can be changed. The skin wrinkles observed on samples stored at 10 ºC are evidence of a higher plant cell dehydration. The observed scratches on blueberry skin samples (Figure II.7) may be owed to mechanical damages during samples preparation (*i.e*. supercritical CO_2 drying) for SEM.

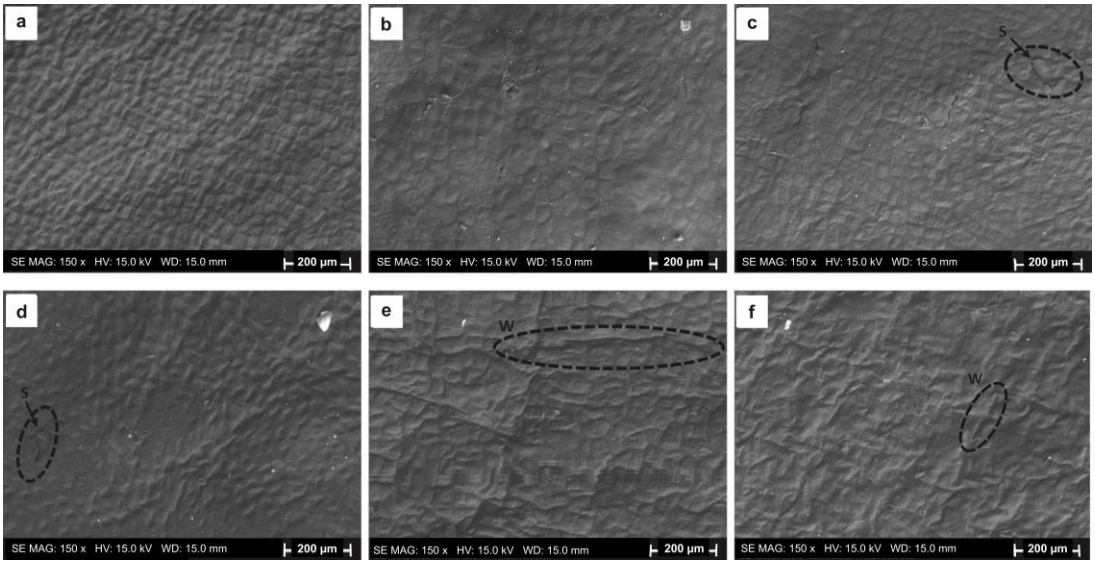


Figure II.7. SEM images of blueberry fruit stored under different packaging conditions at 2 and 10 ºC on day 21. a, b and c correspond to MAP, MAP+COM_{BION} and MAP+PMMT (see Table II.1), respectively, at 2 ºC; d, e and f correspond to MAP, MAP+COM_{BION} and MAP+PMMT, respectively, at 10 ºC. S: shrivel; W: wrinkle (source: Own elaboration).

II.3.6 Firmness

Firmness data was affected ($P \leq 0.001$) by treatments and temperature together with the treatment × temperature interaction ($P \leq 0.01$). Nevertheless, the treatment × temperature × time interaction was no significant ($P > 0.01$) on firmness data. Blueberries showed an initial firmness of 1.96 ± 0.10 N (Table II.2). The firmness of AIR samples was reduced to

1.44 ± 0.03 N after 21 days at 10 ºC. Likewise, it has been previously observed that the softening of blueberries is intensified as the weight loss is increased (Paniagua et al., 2013). Nonetheless, storage at 2 ºC highly controlled firmness loss in AIR samples, showing similar firmness results to those obtained for blueberries stored under MAP conditions at the same storage temperature up to 46 days.

II.3.7 Physicochemical quality

II.3.7.1 Soluble solids content, pH and titratable acidity

Blueberries showed initial SSC and TA of 9.8 ± 0.1 % and 7.5 ± 0.6 g L^{-1}, respectively (Table II.2). After 21 days of storage, the SSC was decreased throughout the remaining storage period, without a significant ($P > 0.05$) difference between storage temperatures. Treatments did not show a high effect ($P > 0.01$) on the SSC. Meanwhile, significant ($P \leq 0.001$) differences among treatments were found on the TA changes during storage. The treatment × temperature interaction was also found to be significant ($P \leq 0.001$) on TA data.

The treatment × temperature × time interaction was found to be significant for both SSC ($P \leq 0.01$) and TA ($P \leq 0.001$). The MI increased over storage time for all treatments, showing significant ($P \leq 0.001$) differences among treatments. The MI was ($P \leq 0.001$) affected by the storage temperature, observing the lowest MI at 2 ºC. A significant ($P \leq 0.001$) treatment × temperature × time interaction was found to be significant for the MI.

A typical SSC increase/TA decrease was generally observed after 7–14 days for all samples. This behaviour is due to fruit ripening processes where sugars are formed while organic acids are used by such metabolic processes. Blueberries stored using C_2H_4 scrubbers showed lower SSC than the remaining treatments without high differences between MAP+COM_{BION} and MAP+PMMT samples. The latter fact may be explained since the C_2H_4 removal in MAP+COM_{BION} and MAP+PMMT samples leads to lower ripening–related metabolic rates and, consequently, to smaller SSC changes. Lower SSC has been also reported in blueberries treated with 1–MCP, although no effect was observed on blueberry TA (Chiabrando & Giacalone, 2011). On the other hand, the TA of MAP samples at 2 ºC was initially better preserved. The latter finding was not observed in those samples stored at 10 ºC. It may be explained by better organic acid preservation at a lower storage temperature together with the reduced O_2 concentration achieved under MAP. Attending to MI, blueberries showed an initial value of 13.0 ± 1.0. The maximum MI increase (19.3 ± 1.7) was found in AIR samples stored at 10 ºC (Table II.2). Blueberries showed an initial pH of 3.13 ± 0.06 that remained with low changes (≤ 0.14 pH units) during storage (Table II.3).

Table II.3. Skin colour, pH and decay incidence of blueberry fruit stored under different packaging conditions (see Table II.1) during storage at 2 and 10 ºC up to 46 days (mean (n=5)±standard deviation) (source: Own elaboration).

Storage Time	Temperature	Treatment	Skin colour (ΔE*)	pH
Processing day			0.00 ± 0.00	3.13 ± 0.06
Day 7	2 ºC	AIR	2.82 ± 1.85	3.10 ± 0.10
		MAP	2.90 ± 1.08	3.03 ± 0.12
		MAP+COM_{BION}	3.81 ± 1.19	3.20 ± 0.10
		MAP+PMMT	3.34 ± 1.25	3.07 ± 0.12
	10 ºC	AIR	3.09 ± 1.41	3.27 ± 0.06
		MAP	3.24 ± 1.64	3.10 ± 0.10
		MAP+COM_{BION}	3.68 ± 1.28	3.10 ± 0.17
		MAP+PMMT	3.20 ± 1.41	3.07 ± 0.06
Day 14	2 ºC	AIR	2.56 ± 0.02	3.17 ± 0.21
		MAP	0.97 ± 0.53	2.97 ± 0.06
		MAP+COM_{BION}	1.67 ± 1.48	3.10 ± 0.10
		MAP+PMMT	0.93 ± 0.32	2.97 ± 0.06
	10 ºC	AIR	2.26 ± 0.86	3.27 ± 0.21
		MAP	3.54 ± 0.76	3.07 ± 0.15
		MAP+COM_{BION}	3.37 ± 0.93	3.20 ± 0.00
		MAP+PMMT	2.41 ± 0.12	3.10 ± 0.10
Day 21	2 ºC	AIR	1.38 ± 0.87	3.15 ± 0.05
		MAP	2.19 ± 0.80	3.00 ± 0.00
		MAP+COM_{BION}	4.16 ± 0.57	3.10 ± 0.10
		MAP+PMMT	2.95 ± 0.17	3.00 ± 0.00
	10 ºC	AIR	2.64 ± 0.72	3.35 ± 0.05
		MAP	3.30 ± 0.55	3.15 ± 0.05
		MAP+COM_{BION}	3.77 ± 1.00	3.10 ± 0.10
		MAP+PMMT	4.00 ± 1.07	3.25 ± 0.05

Table II.3. Continued.

Storage Time	Temperature	Treatment	Skin colour (ΔE*)	pH
Day 46	2 ºC	AIR	2.37 ± 0.00	3.10 ± 0.00
		MAP	3.28 ± 0.00	3.20 ± 0.00
		MAP+COM_{BION}	3.43 ± 0.00	3.10 ± 0.00
		MAP+PMMT	3.62 ± 0.00	3.10 ± 0.00
	10 ºC	AIR	—	—
		MAP	3.88 ± 0.00	3.10 ± 0.00
		MAP+COM_{BION}	3.23 ± 0.00	3.30 ± 0.00
		MAP+PMMT	2.79 ± 0.00	3.20 ± 0.00
	Gas treatment (A)		(0.70)‡	(0.08)‡
	Temperature (B)		(0.28)*	(0.05)‡
	Time (C)		(0.75)‡	(0.08)‡
	A×B		(0.57)*	(0.11)‡
	A×C		(1.49)‡	(0.17)‡
	B×C		(1.06)‡	(0.12)‡
	A×B×C		ns	(0.24)‡

Values within parentheses represent the least significant difference.
ns, *, †, ‡ significance for $P \leq$ not significant, 0.05, 0.01, and 0.001, respectively.

Blueberry harvest is usually done when 15–25 % of the fruit on a bush has turned blue to ensure a high postharvest quality of this fruit. Nevertheless, the early harvest of blueberries alters the full flavour development process (Lobos et al., 2014). One of the most typical sensory attributes of blueberries is a well–balanced content of sugars and organic acids, which is reflected in their sweet slightly acidic taste. According to SSC and TA, blueberries could be harvested closer to their optimum ripening quality since long postharvest storage can be ensured using the C_2H_4 scrubbers. According to Ballinger et al. (1978) recommendations, the maximum MI of our samples could still guarantee a long transport of blueberries like transatlantic shipping. Ballinger et al. (1978) suggested a classification of blueberry fruit for international export markets based on MI. They recommended a blueberry MI ≤ 20 for transatlantic shipping (journeys>7–10 days) and a 20 < MI < 27 for

transcontinental shipping (journeys over 4–5 days), while blueberry fruit with a 27 ≤ MI ≤ 30 is recommended for the local market.

II.3.7.2 Skin colour

The blueberries skin colour did not highly change (ΔE*< 2.7) during storage (Table II.3). Therefore, such ΔE* may not be appreciated by the human eye as corroborated by the sensory analyses (see section II.3.9). Similarly, no high colour differences were observed in blueberries during storage at 4–5 ºC (Abugoch et al., 2016; Moreno et al., 2007). The fresh blueberry colour is highly determined by the skin bloom rather than by the anthocyanin content of the blueberry skin (Abugoch et al., 2016; Sapers et al., 1984). Nevertheless, since skin bloom was removed prior to colour measurements (as justified in the methodology), blueberry skin colour in this experiment was mainly influenced by the changes of the anthocyanin contents of the blueberries skin during storage.

II.3.8 Decay Incidence and microbial growth

II.3.8.1 Decay incidence

The storage temperature had a significant effect ($P \leq 0.001$) on the decay incidence of blueberries. Decay incidence was also affected ($P \leq 0.001$) by treatments. In fact, significant ($P \leq 0.001$) differences between MAP+COM_{BION} and MAP+PMMT samples were observed after 46 days at 10 ºC with 38.1 ± 0.0 and 25.3 ± 0.0 % decayed fruit (Table II.3), respectively. Furthermore, a significant ($P < 0.001$) treatment × temperature interaction was observed on decay incidence data. The treatment × temperature × time interaction was also found to be significant ($P \leq 0.001$) on decay incidence data. Decayed fruit among AIR samples ranged from approximately 3 to 12 % from day 7 to day 21 at 2 ºC (Table II.2). The decay incidence of AIR samples increased to almost 18 % after 46 days at 2 ºC. However, when AIR samples were stored at 10 ºC a decay incidence of 7.9 ± 0.3 % was already observed on day 7, being progressively increased up to 52.6 ± 0.5 % at day 21. The decay incidence was controlled by the MAP technique with an incidence of 9.1 ± 0.9 % in MAP samples after 21 days at 10 ºC. The MAP effect on blueberry decay incidence was even increased when these samples were stored at 2 ºC showing a decay incidence lower than 6 % after 21 days at 2 ºC. Then, the storage of blueberries at 2 ºC controlled the decay incidence in this fruit. It may be explained since fungal growth is reduced as the storage temperature is reduced (Paniagua et al., 2014). Meanwhile, the MAP beneficial effect on fruit decay may be owed to the achieved CO_2 partial pressures (4.4–9.8 mmol L^{-1}), which effectively control the decay incidence in blueberries (Terry et al., 2009).

Fungal decay was even controlled by the incorporation of C_2H_4 scrubbers (Table II.2). This finding may be attributed to C_2H_4 removal since C_2H_4 can promote fungi growth (Zhu et al., 2012). The observed differences between decay incidence of MAP+COM_{BION} and MAP+PMMT samples during storage at 10 ºC may be due to the low CO_2 concentrations within MAP+COM_{BION} samples. Then, fungal decay incidence in blueberry fruit was controlled for 21 days at 10 ºC under MAP, and 46 days at 2 ºC, but when C_2H_4 scrubbers were incorporated into the blueberry packages a better decay control could be reached.

II.3.8.2 Microbial growth

The Y+M loads were significantly affected ($P \leq 0.001$) by treatments; but no for psychrophilic ($P > 0.01$), *Enterobacteriaceae* ($P > 0.05$) or mesophilic ($P > 0.05$) counts (Table II.4). Storage temperature showed a significant ($P \leq 0.001$) effect on both psychrophilic and mesophilic counts, but no effect ($P > 0.05$) was observed on the *Enterobacteriaceae* counts. No high differences ($P > 0.01$) were found between both storage temperatures for Y+M counts. Similarly, no high Y+M growth was observed between the storage of blueberries stored either at 4 or 12 ºC (air conditions) for 10 days (Concha-Meyer et al., 2015). The unchanged Y+M growth at higher refrigeration temperatures in blueberries has been reported to be due to the antimicrobial properties of the skin bloom, which is highly appreciated by consumers (Cline, 1996). A significant interaction ($P \leq 0.01$) among treatments, temperature and storage time for psychrophilic counts was observed. Contrary, the evaluated factors (treatments, temperature and storage time) showed no significant interactions on Y+M ($P > 0.05$), *Enterobacteriaceae* ($P > 0.05$) or mesophilic counts ($P > 0.01$).

Table II.4. Microbial load of blueberry fruit stored under different packaging conditions (see Table II.1) during storage at 2 and 10 ºC up to 46 days for 21 and 46 days, respectively (mean (n=5)±standard deviation) (source: Own elaboration).

Storage Time	Temperature	Treatment	Mesophiles	Psychrophiles	Enterobacteriaceae	Y+M
Processing day			3.2 ± 0.3	3.8 ± 0.1	2.8 ± 0.1	3.1 ± 0.2
Day 7	2 ºC	AIR	3.3 ± 0.5	4.0 ± 0.6	2.4 ± 0.3	3.8 ± 0.2
		MAP	2.9 ± 0.3	3.8 ± 0.3	2.6 ± 0.1	3.6 ± 0.1
		MAP+COM_{BION}	2.8 ± 0.1	3.0 ± 0.3	2.7 ± 0.1	3.7 ± 0.2
		MAP+PMMT	3.3 ± 0.2	2.8 ± 0.5	2.6 ± 0.1	3.5 ± 0.1
	10 ºC	AIR	3.5 ± 0.3	4.1 ± 0.5	2.5 ± 0.0	3.8 ± 0.1
		MAP	3.3 ± 0.2	4.0 ± 0.5	3.2 ± 0.7	3.8 ± 0.1
		MAP+COM_{BION}	3.2 ± 0.3	3.7 ± 0.3	2.8 ± 0.3	3.4 ± 0.3
		MAP+PMMT	3.3 ± 0.5	3.2 ± 0.2	3.4 ± 0.9	3.9 ± 0.2
Day 14	2 ºC	AIR	3.0 ± 0.0	2.9 ± 0.1	2.5 ± 0.3	3.6 ± 0.2
		MAP	2.6 ± 0.0	2.9 ± 0.4	2.0 ± 0.1	3.5 ± 0.1
		MAP+COM_{BION}	2.7 ± 0.1	2.6 ± 0.3	1.8 ± 0.3	3.5 ± 0.1
		MAP+PMMT	3.3 ± 0.2	2.8 ± 0.3	2.0 ± 0.2	3.2 ± 0.2
	10 ºC	AIR	3.7 ± 0.2	3.2 ± 0.6	2.5 ± 0.2	3.6 ± 0.1
		MAP	3.2 ± 0.1	3.3 ± 0.4	2.0 ± 0.0	3.4 ± 0.1

Table II.4. Continued.

Storage Time	Temperature	Treatment	Mesophiles	Psychrophiles	Enterobacteriaceae	Y+M
		MAP+COM_{BION}	3.6 ± 0.3	3.3 ± 0.1	2.5 ± 0.1	3.5 ± 0.2
		MAP+PMMT	3.2 ± 0.2	3.3 ± 0.3	2.2 ± 0.3	3.3 ± 0.1
Day 21	2 ºC	AIR	3.3 ± 0.4	3.5 ± 0.1	3.5 ± 0.2	3.2 ± 0.1
		MAP	3.9 ± 0.6	3.2 ± 0.0	3.3 ± 0.1	3.1 ± 0.1
		MAP+COM_{BION}	3.6 ± 0.5	3.9 ± 0.1	3.2 ± 0.2	3.0 ± 0.1
		MAP+PMMT	3.5 ± 0.3	3.7 ± 0.1	3.2 ± 0.1	3.0 ± 0.1
	10 ºC	AIR	4.2 ± 0.3	4.6 ± 0.1	2.5 ± 0.2	3.6 ± 0.1
		MAP	3.5 ± 0.0	4.4 ± 0.0	3.0 ± 0.0	3.0 ± 0.1
		MAP+COM_{BION}	3.6 ± 0.1	4.3 ± 0.1	3.3 ± 0.1	3.2 ± 0.1
		MAP+PMMT	3.7 ± 0.0	4.6 ± 0.1	3.3 ± 0.1	3.3 ± 0.0
Day 46	2 ºC	AIR	3.8 ± 0.0	4.5 ± 0.0	4.5 ± 0.0	2.8 ± 0.0
		MAP	4.0 ± 0.0	4.8 ± 0.0	4.5 ± 0.0	2.6 ± 0.0
		MAP+COM_{BION}	3.6 ± 0.0	4.6 ± 0.0	4.6 ± 0.0	2.5 ± 0.0
		MAP+PMMT	3.6 ± 0.0	4.5 ± 0.0	4.4 ± 0.0	2.9 ± 0.0
	10 ºC	AIR	—	—	—	—
		MAP	—	—	—	—

Table II.4. Continued.

Storage Time	Temperature	Treatment	Mesophiles	Psychrophiles	Enterobacteriaceae	Y+M
		$MAP+COM_{BION}$	—	—	—	—
		MAP+PMMT	—	—	—	—
	Gas treatment (A)		ns	(0.1)*	ns	(0.2)‡
	Temperature (B)		(0.2)‡	(0.2)‡	ns	(0.1)*
	Time (C)		(0.3)‡	(0.3)‡	(0.3)‡	(0.2)‡
	A×B		(0.2)*	ns	ns	ns
	A×C		ns	(0.5)‡	(0.3)*	ns
	B×C		(0.2)*	(0.4)‡	(0.2)*	ns
	A×B×C		(0.4)*	(0.6)†	ns	ns

Y+M: Yeast and moulds sum.
Values within parentheses represent the least significant difference.
ns, *, †, ‡ significance for $P \leq$ not significant, 0.05, 0.01, and 0.001, respectively.

Blueberries showed initial Y+M, psychrophilic, mesophilic and *Enterobacteriaceae* counts of 3.1 ± 0.2, 3.8 ± 0.1, 3.2 ± 0.3 and 2.8 ± 0.1 log CFU g^{-1} (Table II.4), respectively. The Y+M counts of AIR samples remained unchanged after 21 days at 10 ºC. An initial Y+M increase of 0.4–0.8 log units was observed after 7 days. Concerning psychrophiles and *Enterobacteriaceae*, a general counts decrease was observed after 7 days.

Nevertheless, psychrophilic loads increased after 14 days from 2.6 to 2.9 log CFU g^{-1} (2 °C) and 3.2 to 3.3 log CFU g^{-1} (10 ºC). Meanwhile, *Enterobacteriaceae* counts increased from 1.8 to 2.0 log CFU g^{-1} (2 °C) and from 2.0 to 2.5 log CFU g^{-1} (10 ºC) after 10 days. The observed behaviour may be owed to an initial microbial adaptation to the new packaging environment and to the temperature conditions being then microbial loads increased without high differences among treatments (Table II.4). The mesophilic count showed an initial mild increase reaching stable loads on day 21.

In general, only Y+M counts were significantly affected by treatments, which agrees with the fungal decay incidence data (Table II.2). As previously discussed, these results can be attributed to the atmosphere composition achieved in MAP blueberries together with the use of C_2H_4 scrubbers. Nevertheless, psychrophilic and mesophilic counts were affected ($P \leq 0.001$) by storage temperatures. All microbial groups remained below 5 log CFU g^{-1} in all samples at the end of the studied storage periods. The low microbial counts of blueberry samples are consistent with reported data being highly attributed to the waxy bloom on the blueberry skin (Cline, 1996; Concha-Meyer et al., 2015).

II.3.9 Sensory quality

Blueberry sweetness is one of the most expected sensory attributes by consumers of this fruit. The highest sweetness scores were observed in AIR samples among the rest of the treatments after 7 days at 10 ºC (Figure II.8). Although AIR samples did not show the highest SSC on day 7, AIR samples reached the lowest TA, which led to the perceived higher sweetness. Good sensory scores were still scored for AIR samples after 14 days at 10 ºC (Figure II.8) but these samples achieved a high decay incidence (as previously commented). The shelf–life of AIR samples may be then established in 7 days at 10 ºC. The high weight losses (> 5 % after 46 days at 2 ºC) may lead to establishing the shelf–life of AIR samples in at least 21 days at 2 ºC. Blueberry sweetness and aroma scores increased throughout storage due to the ripening processes while the blueberry texture was reduced (according to firmness data). Samples stored at higher temperatures developed more volatile aromas as observed in the aroma scores of samples after 21 days (Figure II.8). Focussing on the C_2H_4 scavenger effects on the sensory quality, MAP+PMMT samples

stored at 2 ºC showed the highest texture and sweetness scores, as well as the lowest skin wrinkling after 21 days.

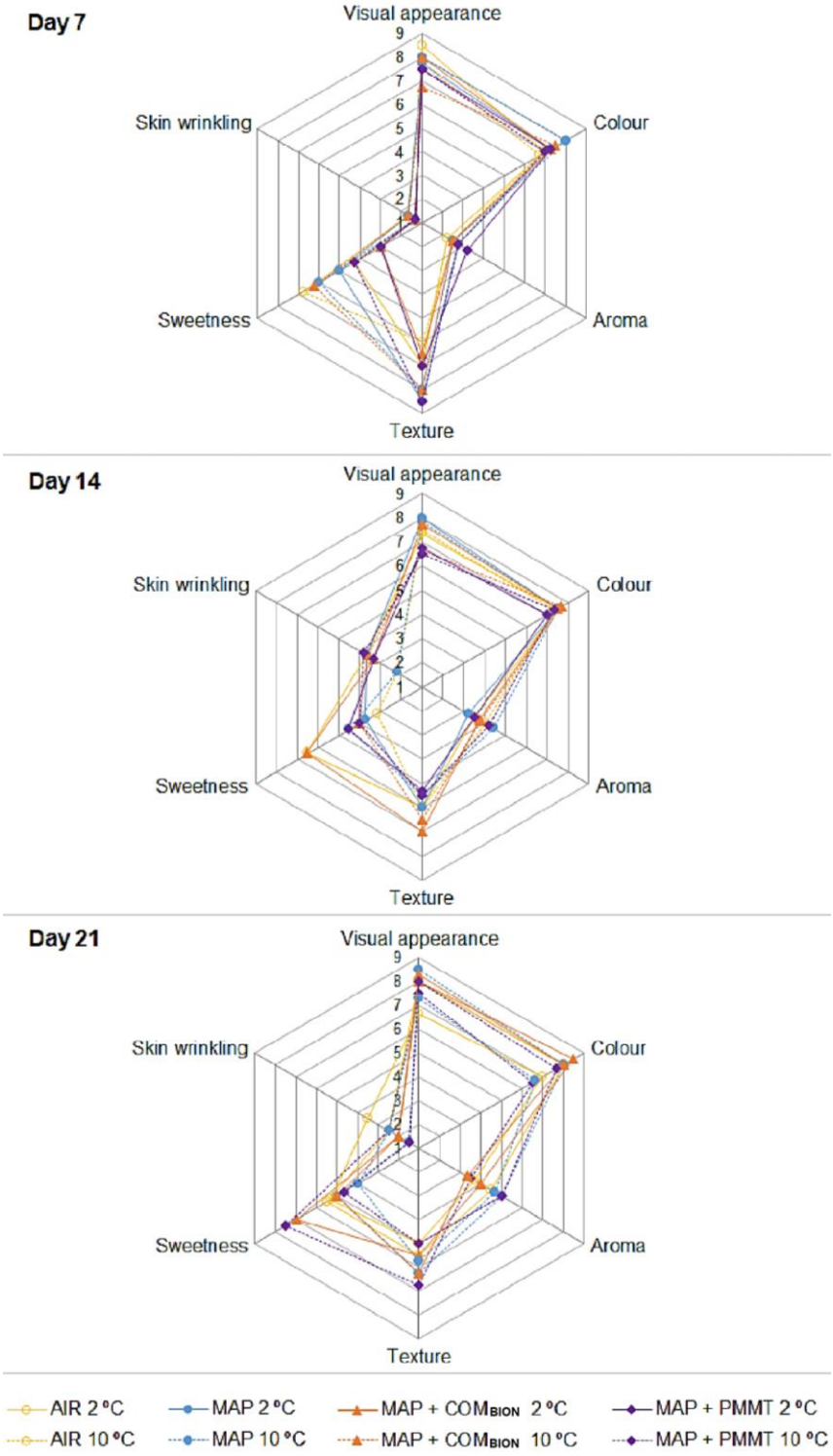
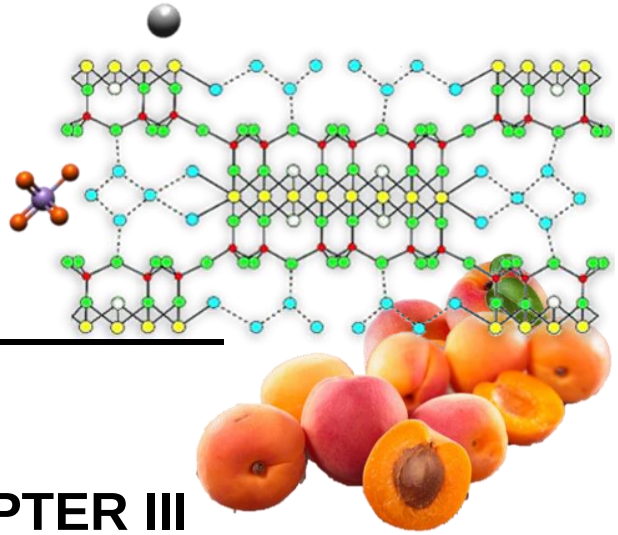


Figure II.8. Sensory quality of blueberry fruit stored under different packaging conditions (see Table II.1) at 2 and 10 ºC on days 7, 14 and 21 (mean (n=5)) (source: Own elaboration).

II.4 Conclusions of this chapter

The developed C_2H_4 scrubber, consisting of a protonated MMT loaded with $KMnO_4$, did not show alterations on the blueberry postharvest quality attributes evaluated. Furthermore, it was found to inhibit fungal decay incidence on fresh blueberry stored under MAP conditions at low storage temperature (2 ºC). Overall, the use of the developed $KMnO_4$–based C_2H_4 scrubbers in conjunction with MAP (1.5 mmol L^{-1} O_2 + 5.3 mmol L^{-1} CO_2 at 2 ºC and 0.7 mmol L^{-1} O_2 + 7.1 mmol L^{-1} CO_2 at 10 ºC) may extend the shelf-life of 'Duke' blueberry (*Vaccinium corymbosum*) fruit, in comparison with that shelf–life reached under air conditions (from 7 days to 21 days at 10 ºC; from 21 days to 46 days at 2 ºC).

The developed C_2H_4 scrubber can be considered an easy–to–use packaging technology with high cost-effectiveness since similar effects to those obtained by using a commercial $KMnO_4$–based material were achieved with less quantity of material. Therefore, the innovative C_2H_4 scrubber seems to be a promising solution for the blueberry market to provide an extended shelf–life product to consumers. However, further research is encouraged for treatment and modification of support materials for C_2H_4 scrubbers (for example, the concentration of the acid used for the protonation process, acidification time, exposure temperatures during swelling, drying and impregnation processes, etc.), with the aim to get an optimized C_2H_4 scrubber material with higher C_2H_4 removal capacity/efficiency.



CHAPTER III

Postharvest Quality Retention of Apricots by Using a Novel Sepiolite–Loaded Potassium Permanganate Ethylene Scavenger

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CHAPTER III. POSTHARVEST QUALITY RETENTION OF APRICOTS BY USING A NOVEL SEPIOLITE–LOADED POTASSIUM PERMANGANATE ETHYLENE SCAVENGER

III.1 Introduction

The clay SP has also been shown great potential for effective C_2H_4 removal (Alver & Sakizci, 2012; Sakizci, 2013). Such clay is a fibrous clay composed of a magnesia sheet enclosed by two tetrahedral silica sheets (Ruiz-Hitzky et al., 2013). SP has a high adsorptive capacity for C_2H_4, which is due to the presence of microporous channels along the SP fibre axis (Alver & Sakizci, 2012). Furthermore, it has been found that acid treatment of SP can improve its C_2H_4 adsorption properties by increasing the surface area and porosity (Alver & Sakizci, 2012; Sakizci, 2013). Because of its nature, SP is non–toxic, inexpensive and eco–friendly (Álvarez-Hernández et al., 2018; Ruiz-Hitzky et al., 2013). Such properties make SP an outstanding natural resource for $KMnO_4$ carrier applications. However, the use of $KMnO_4$ with SP in post-harvest storage systems has been scarcely reported. De La Plaza et al. (2003) showed that, during storage at subcritical temperature, ripening and oxidative degradation of unsaturated fatty acids of 'Hass' avocado can be delayed by using $KMnO_4$–impregnated SP in a closed system of forced air. In another study, Taboada-Rodríguez et al. (2013) modified cardboard surface with polylactic acid coatings containing particles of SP–$KMnO_4$. The last authors focused on the H_2O barrier properties of the coated cardboard, while the C_2H_4 scavenging properties were not studied.

Apricot (*Prunus armeniaca* L.) is a palatable stone fruit, rich in nutritional and health-promoting compounds (Muzzaffar et al., 2018). Nowadays, apricot production is a relevant economic activity in the Mediterranean countries, which have high socio-economic importance in food supply and global markets (FAO, 2019a; FEPEX, 2019). Nevertheless, apricot shelf–life can be shortened by the presence of C_2H_4 during distribution and storage (Fan et al., 2018; Leida et al., 2011). In fact, apricot flesh firmness was significantly affected by exogenous C_2H_4 (Palou & Crisosto, 2003). Several studies have shown the potential of $KMnO_4$–based C_2H_4 scavengers for reducing C_2H_4 release and fruit firmness loss of apricots during storage at low temperatures (Li et al., 2018; Palou & Crisosto, 2003). Furthermore, Ali et al. (2015) reported that biochemical composition changes, antioxidant activity decrease and enzyme activities of 'Habi' apricot were slowed down during room temperature storage employing C_2H_4 scavenging technology based on $KMnO_4$.

This experiment aimed to study the effects of a novel $KMnO_4$–based C_2H_4 scavenger supported with a pre-treated SP on the postharvest quality of fresh apricots. Because

atmospheric packaging conditions and storage temperature can affect the performance of C_2H_4 scavengers, the study was carried out under MAP and air conditions at 2 and 15 ºC, respectively. The novel scavenger was characterized and its effects on apricot postharvest quality were compared with those obtained through a commercial one ($KMnO_4$ onto natural clays, including zeolite). To the best of our knowledge, no other studies have addressed the effects of a C_2H_4 scavenger made of $KMnO_4$ supported on SP on postharvest apricot quality during storage.

III.2 Material and methods

III.2.1 Plant and chemical materials

Apricot (*Prunus armeniaca* L. var. Mirlo naranja) was grown in an open-air cultivation parcel in the south of Spain by the company Frutas Esther, S.A. (Abarán, Murcia, Spain) according to integrated pest management cultural practices. Approximately 110 kg of apricot fruit was hand-harvested in May 2018 during the early morning. Apricots were harvested at a deep orange/red ripening stage, with some pale–yellow colour remaining on the fruit skin. Then, apricots were transported by car to the UPCT and stored in a cold room (2 ºC, 90–95 % RH) for 3 days to ensure a stabilized fruit metabolism and cool down its harvesting temperature. Apricots were sorted to select those with uniformity in size and skin colour, and free from defects.

The $KMnO_4$ and HCl (36–38 %) reagents were acquired from Sigma–Aldrich (Germany) while SP (15/30 mesh) was acquired from Bolaseca (Torres de Cotillas, Murcia, Spain). Bi–On® R12 (Bioconservacion S.A., Barcelona, Spain) was used as the commercial C_2H_4 scavenger (granules in cylindrical pellet form) according to be one of the commercial scavengers with the best performance (Álvarez-Hernández et al., 2019). Tyvek® film (220 µm thickness; DuPont, Wilmington, DE, USA) was used to prepare all the C_2H_4 scavenger sachets due to its high gas permeation with low H_2O vapour permeability. All solutions were prepared using distilled H_2O.

III.2.2 Preparation of the treated sepiolite–supported potassium permanganate ethylene scavenger

A novel C_2H_4 scavenger was developed using $KMnO_4$ as the active ingredient and treated SP as the $KMnO_4$ support. First, dried SP (60 ºC) was washed and purified by an acidification process as follows: 1) a 5 % *w/v* SP:H_2O dispersion was prepared and mixed at 70 ºC for 3 h; 2) the SP dispersion was kept overnight with constant stirring at 30 ºC; 3)

the dispersion was heated to 80 ºC and a 25 mM HCl solution was added at a concentration of 33 % v/v HCl:SP dispersion; 4) the resulting solution was stirred at 80 ºC for 2 h and then centrifuged at 3,500×g for 15 min. The solid phase was recovered and washed several times with distilled H_2O until the elimination of chloride ions, which was indicated by a pH ≈ 7. Finally, the obtained precipitate was dried at 110 ºC for 14 h. The obtained treated SP was ground at 18.0 1 s^{-1} for 2 min in a ball mill (MM 200; Retsch GmbH & Co. KG, Haan, Germany). Finally, the SP–supported $KMnO_4$ material was prepared according to the procedure previously reported (Álvarez-Hernández et al., 2019). Briefly, a 5 % *w/v* SP: H_2O dispersion was heated at 70 ºC for 3 h and the resulting suspension was mixed with a concentrated $KMnO_4$ solution (6.4 % $KMnO_4$) in a 1:12.8 $KMnO_4$:SP ratio (*w/w*). After the modification process, the resulting slurry was dried at 60 ºC and then ground in the ball mill as described above. The obtained clay powder was referred to as SK.

III.2.3 Characterization of the developed ethylene scavenger

Morphological characterization was performed by a FE-SEM (SU8010, Hitachi instrument, Tokyo, Japan). Prior to SEM, samples were mounted on aluminium discs and coated with gold in a sputter coater (SC7640, Quorum Technologies, East Sussex, UK) to make their surfaces electrically conductive. The crystalline phases were also identified using a Bruker D8 Advance powder XRD system (Billerica MA, USA). Reflexion patterns were matched to the ICDD PDF–4+ 2018 database for phase identification. The materials were also characterized by WDXRF spectrometry using a XRF Spectrometer (Bruker AXS S4; Pioneer, Billerica MA, USA) to determine their chemical composition.

III.2.4 Ethylene and carbon dioxide production

Apricot samples (256.7 ± 13.5 g) were selected for uniformity without any damage and placed into 1–L glass jars for C_2H_4 and CO_2 production determinations. The experiment was performed at 2 and 15 ºC based on the procedure described by Martínez-Hernández et al. (2011). Five replicates (5 jars) per storage temperature were prepared and then subjected to a continuous humidified airflow (20 mL min^{-1}) to keep CO_2 concentrations below 0.13 mmol L^{-1} inside the jars (Watada, 1986) avoiding alteration of metabolic respiration processes. Apricot samples were allowed to stabilize and acclimate during 15 h at the setup test conditions. After that, C_2H_4 and CO_2 production measurements were performed daily during 14 days.

At each measurement day, the jars were airtight sealed for 2 h, and a gas sample (1 mL) was drawn and injected into the corresponding GC instrument as follows: for C_2H_4 determinations, a GC instrument (7820A GC System, Agilent Technologies, Santa Clara

CA, USA) equipped with a FID and a stainless–steel column packed with Porapak Q (1/8", 80/100 mesh size; Teknokroma, Barcelona, Spain) was used. The oven, injector and detector temperatures were 80, 120 and 250 ºC, respectively. Air and H_2 were used as gas carriers at 350– and 30–mL min^{-1}, respectively. Meanwhile, a GC instrument (Clarus 500 GC; PerkinElmer Inc., Shelton CT, USA) equipped with a TCD and a stainless–steel column packed with Hayesep Q (1/8", 80/100 mesh size; Teknokroma, Barcelona, Spain) followed by a stainless–steel column packed with molecular sieve 5A (1/8", 80/100 mesh size; Teknokroma, Barcelona, Spain) was used for CO_2 and O_2 measurements. The oven, injector and TCD temperatures were 60, 100 and 150 ºC, respectively. Air and H_2 were used as gas carriers at 20– and 2–mL min^{-1}, respectively.

After taking the air sample, the jars were opened and reconnected to the airflow. Five measurements per jar were daily assayed. The production of C_2H_4 and CO_2 was expressed as pmol kg^{-1} s^{-1} and nmol kg^{-1} s^{-1}, respectively.

III.2.5 Packaging treatments

The packaging process was carried out in a disinfected cold room at 8 ºC. Apricots (515.6 ± 4.9 g; 8 units) were placed in 2–L rigid PP trays, which were then heat-sealed on the top with an oriented PP film (35 µm thickness; 174,213– and 175,341–mL m^{-2} day^{-1} atm^{-1} for O_2 and CO_2 permeabilities, respectively, at 10 °C and 0 % RH; Plásticos del Segura, Murcia, Spain). Prior to heat–sealing, one C_2H_4 scavenger sachet (6.0 × 6.5 cm), containing either 1 g of the commercial scavenger (hereinafter referred to as COM_{BION}) or 0.5 g of the developed one (SK), were attached at the centre of each film (on the inner side), using double-sided tape. To get a similar C_2H_4 removal (%), the C_2H_4 scavenger quantities per sachet were adjusted according to the breakthrough curves (Figure III.1), which were obtained as previously indicated (Álvarez-Hernández et al., 2019). Apricots packed without C_2H_4 scavengers were used as controls in AIR or MAP conditions.

Apricot trays were kept at either 2 or 15 ºC in a 27.47–m^3 cold storage room (2.70 x 3.70 x 2.75 m) equipped with an air–cooling system and humidifiers (Tecnidex, Valencia, Spain). Although the optimum storage temperature for apricots is -0.5 to 0 ºC (Crisosto et al., 1998), 2 ºC was selected to avoid freezing problems in the cold room evaporators. The 15 ºC–storage temperature was selected since refrigeration needs for apricot could be reduced utilizing C_2H_4 scavengers (Botondi et al., 2000). While a MAP was developed during the storage of samples at 2 ºC, trays stored at 15 ºC were previously cut across on one side (achieving air conditions) to allow environmental atmospheric conditions. The assessed apricot packaging and the performed storage conditions, as applied treatments, are

summarized in Table III.1. Three trays (replicates) were prepared per each packaging treatment, storage temperature and sampling time (105 trays in total).

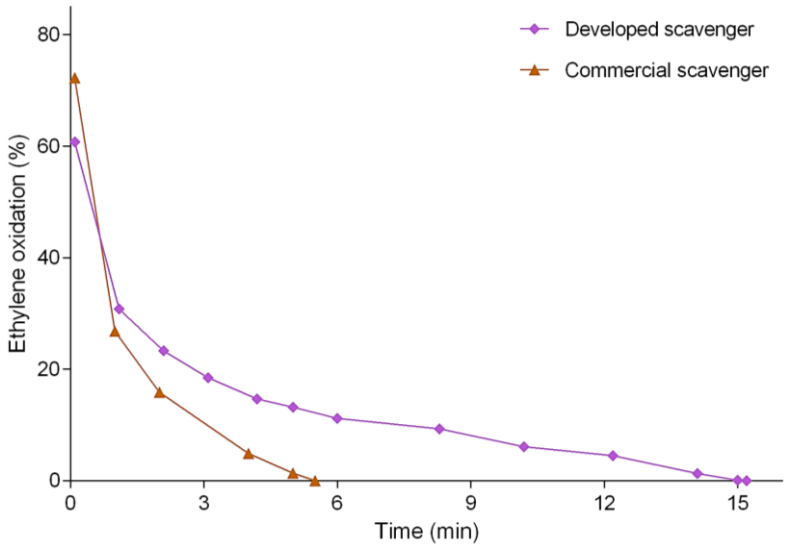


Figure III.1. Breakthrough curves of ethylene oxidation by the commercial (♦) and the developed $KMnO_4$–based C_2H_4 scavenger (▲) overtime at an ethylene flow rate of 140 mL min^{-1} (source: Own elaboration).

Main physicochemical traits that influence consumer acceptability of apricot were evaluated as quality indexes during fruit storage (Crisosto et al., 1998; Muzzaffar et al., 2018) after 0 (processing day), 8, 15, 22, 29 and 36 days (2 ºC) and 0, 8, 11, 14, 17, and 20 days (15 ºC). Prior to quality appraisals, apricot samples to be analysed were left to acclimate at room temperature for 1 h.

III.2.6 Gas composition during modified atmosphere packaging

The MAP gas composition was constantly monitored during storage. Gas samples (1 mL) were withdrawn from the package headspace using a syringe and then injected into the correspondent GC instrument with the same GC conditions as described above. Five measurements per package were made every sampling day. The CO_2 and O_2 concentrations in the packaging atmosphere were expressed in terms of mmol L^{-1}, whereas the C_2H_4 concentration was expressed as nmol L^{-1}.

III.2.7 Fruit quality attributes

III.2.7.1 Weight loss

Apricot weight loss was monitored during storage using an analytical balance (Ohaus EX124; Parsippany, New Jersey, USA). The same samples were used at each sampling

time throughout the experiment. Fruit weight loss was expressed as the percentage difference between the initial and the current net weight at each sampling time.

Table III.1 Description of the storage packaging conditions evaluated at 2 and 15 ºC (source: Own elaboration).

Storage temperature	Packaging nomenclature	Packaging conditions
2 ºC	AIR	Air packaging
	MAP	MAP
	MAP+COM_{BION}	MAP with commercial scavenger: Bion R-12 (1 g per sachet)
	MAP+SK	MAP with the developed scavenger: $KMnO_4$ supported on sepiolite (0.5 g per sachet)
15 ºC	AIR	Air packaging
	AIR+COM_{BION}	Air with commercial scavenger: Bion R-12 (1 g per sachet)
	AIR+SK	Air with the developed scavenger: $KMnO_4$ supported on sepiolite (0.5 g per sachet)

MAP: modified atmosphere packaging.

III.2.7.2 Firmness

Firmness changes were determined by performing a compression test using a texture analyser (LFRA–4500; Brookfield AMETEK; Middleboro, MA, USA) with a 25.4–mm diameter (35–mm long) cylinder acrylic probe. Each whole apricot unit, with the peel, was compressed 1 mm on the equatorial region using a test speed of 10 mm s^{-1} and a trigger force of 100 g. The peak force (N) necessary to achieve the target distance was recorded. Firmness was determined on 5 fruits per tray and then averaged.

III.2.7.3 Soluble solids content, pH and titratable acidity

A juice was obtained from apricots using a blender machine. Five apricots per tray were used to obtain a juice sample. SSC was determined from the apricot juice using a digital handheld refractometer (Atago N1; Tokyo, Kanto, Japan) at 20 ºC and expressed as % (sugar equivalents in g 100 g^{-1}). The pH of the juice samples was measured using a pH−meter (Basic20, Crison; Alella, Cataluña, Spain). TA analysis was performed by titrating 50 mL of diluted juice (3 mL juice + 47 mL of distilled H_2O) with 0.1 N NaOH to an endpoint of pH 8.1 using an automatic titrator (T50; Metter Toledo; Milan, Italy). TA was expressed as malic acid equivalents in g L^{-1}. Furthermore, SSC/TA ratio was also calculated.

III.2.7.4 Colour

Apricot skin colour was determined by means of CIE *L*a*b** tristimulus values as previously reported (Álvarez-Hernández et al., 2019). *L**, *a** and *b** values were obtained using a colourimeter (Chroma Meter CM–A131, Minolta; Tokyo, Japan) with 8–mm viewing aperture, CIE standard illuminant D65 and reference angle of 2 º. Measurements were carried out on three different skin points of 5 randomly selected apricots per tray. Before measurements, the colourimeter was calibrated with a white reference plate (illuminant D65). Results were expressed employing the CIE *L*C**H_{ab} colour space, which is a vector representation of the CIE *L*a*b** colour space.

III.2.7.5 Fungal incidence

Fungal incidence was estimated by visual inspection every sampling day on each individual fruit. Apricot fruit showing any visible mycelial development was considered infected. These data were expressed as the percentage of apricots infected.

III.2.7.6 Sensory evaluation

Sensory analyses were performed according to international standards (ASTM, 1986). Sensory tests were conducted in a standard room (ISO_8586:2012; ISO (2012)) equipped with 10 individual tasting booths. Samples were served in white plastic dishes, which had been previously labelled with a random 3–digit code. Still H_2O was used to clean the palate between tested samples. The panel consisted of 10 trained assessors (5 women and 5 men, aged between 22 and 70 years). Appearance, flavour and mouthfeel texture quality and overall acceptability were evaluated using a hedonic scale ranging from 5 to 1 (5: extremely good; 4: moderately good; 3: fair, limit of usability; 2: moderately bad; 1: extremely bad). Furthermore, a 5–point rating scale of damage incidence and severity (5: none; 4: slight; 3: moderate; 2: strong; 1: severe) was used for off−odours and internal browning.

III.2.8 Statistical analysis

The experiment was conducted in a two–factor (fruit packaging condition × storage time) factorial design. ANOVA was performed using SPSS software (v.19 IBM, New York, USA). Mean separations were conducted by the Tukey's multiple range test at a significance level of $P \leq 0.05$.

III.3 Results and discussion

III.3.1 Characterization of the developed ethylene scavenger

The morphology of the purified SP, which was used as $KMnO_4$ support, is shown in Figure III.2a, whereas the morphology of the developed $KMnO_4$–based C_2H_4 scavenger is shown in Figure III.2c. The surface morphology of the $KMnO_4$–based C_2H_4 scavenger was significantly different from that of the $KMnO_4$ support material. A characteristic SP fibrous morphology was found in the $KMnO_4$ support (Zhang et al., 2017). After the C_2H_4 scavenger preparation process, breakage of SP fibres to some degree was observed and fibre bundles decreased in width. Besides, flat flakes appeared on the resulting $KMnO_4$–based C_2H_4 scavenger (as indicated by circles in Figure III.2c), suggesting that a phase transformation took place.

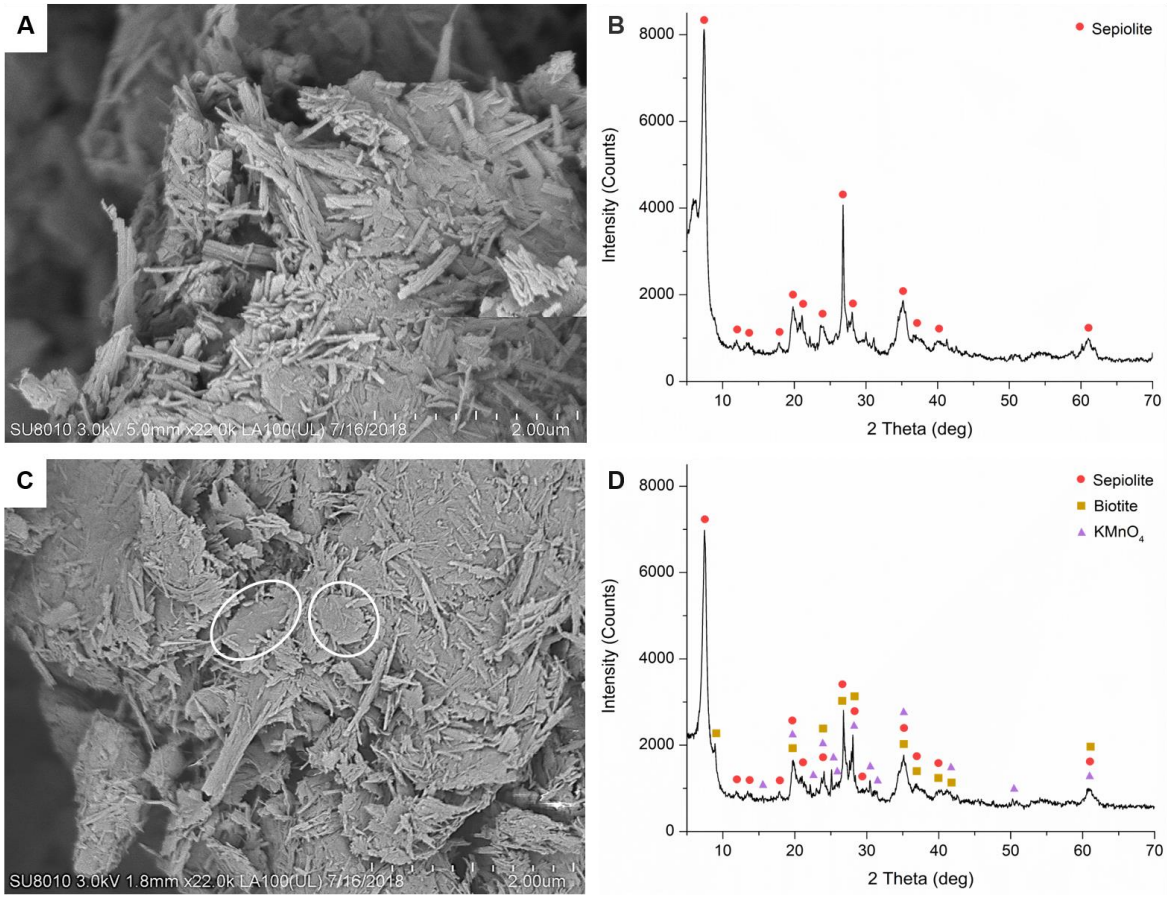


Figure III.2. Scanning electron microscopy images at 22.0 k × magnification of the used $KMnO_4$ support (a) and the developed $KMnO_4$–based C_2H_4 scavenger (c), and their respective powder X-ray diffraction patterns (b, $KMnO_4$ support; d, developed $KMnO_4$–based C_2H_4 scavenger) (source: Own elaboration).

The XRD patterns obtained from the $KMnO_4$ support and the resulting $KMnO_4$–based C_2H_4 scavenger are shown in Figure III.2b and III.1d, respectively. After the SP modification

process with $KMnO_4$, new diffraction peaks were found. According to ICDD PDF–4+ 2018 database, it was confirmed that the main crystal phase in the used $KMnO_4$ support corresponded to SP (ICDD PDF 04–017–9666), whose chemical formula is $Mg_{3.1}Ti_{0.09}Fe_{0.14}Al_{0.34}Si_6O_{15}(OH)_2(H_2O)_5$. Although the $KMnO_4$ support had been previously subjected to a purification process, the XRD patterns showed the presence of some impurities (Figure III.2b). Meanwhile, semi-quantitative XRD analysis revealed that the $KMnO_4$–modified SP consisted of three main crystal phases: 62 % SP, 20 % biotite–1M (ICDD PDF 01–076–6570), and 18 % $KMnO_4$ (ICDD PDF 04–006–5394). These results suggested that $KMnO_4$ was not only supported on SP, but a chemical reaction between both compounds occurred, forming biotite mica $[(K_{1.907}Na_{0.033})(Al_{0.090}Fe_{2.397}Mg_{3.071}Mn_{0.043}Ti_{0.400})((Si_{5.619}Al_{2.381})O_{21.456}(OH)_{2.544})]$, explaining the SEM morphological differences observed between the $KMnO_4$ support and the developed $KMnO_4$–based C_2H_4 scavenger.

The element concentrations of the $KMnO_4$ support and the developed $KMnO_4$–based C_2H_4 scavenger are presented in Table III.2. According to XRD patterns, WDXRF data also indicated that the $KMnO_4$ support used is a hydroxy-containing, magnesium– and silicon-rich compound. Moreover, important increases in the concentrations of K and Mn elements were evidenced when SP was loaded with $KMnO_4$, revealing the $KMnO_4$ incorporation. Nonetheless, decreases were also found in the O_2 and silicon concentrations, changing from 53.16 % to 50.63 % in terms of SiO_2 as a percentage, which could be related to biotite formation during the $KMnO_4$–based C_2H_4 scavenger preparation process as evidenced by the XRD results.

The hereby observed morphological changes between the $KMnO_4$ support and the resulting $KMnO_4$–based C_2H_4 scavenger could be attributed to the decreases in O_2 and silicon concentrations resulting from the C_2H_4 scavenger preparation process (Myriam et al. 1998). On the other hand, Liu et al. (2006) also observed that a phase transformation had taken place during the $KMnO_4$ impregnation process over a silica-alumina-based support. Then, it can be inferred that the biotite presence in the developed $KMnO_4$–based C_2H_4 scavenger implies that interactions between the $KMnO_4$ support material and the $KMnO_4$ occurred.

Table III.2. Element concentration (%) of the $KMnO_4$ support used and the developed $KMnO_4$–based C_2H_4 scavenger (source: Own elaboration).

C_2H_4 scrubber	**H**	**O**	**Na**	**Mg**	**Al**	**Si**	**K**	**Ca**	**Ti**	**Mn**	**Fe**	**Other elements***
$KMnO_4$ support (purified sepiolite)	1.75	54.25	0.16	11.89	3.09	24.85	1.43	0.95	0.15	0.03	1.35	0.01
Developed $KMnO_4$-based C_2H_4 scavenger ($KMnO_4$-modified sepiolite)	1.47	51.56	0.15	11.35	3.27	23.67	3.54	0.64	0.16	2.59	1.50	0.01

*P, S, Cl, V, Cr, Co, Ni, Cu, Zn, Ga, Rb, Sr, Y, Zr, Nb, Ba

III.3.2 Ethylene and carbon dioxide production of apricot fruit

III.3.2.1 Ethylene production

As expected, the C_2H_4 production of apricots stored at 2 ºC was significantly ($P \leq 0.001$) lower than that of the apricots stored at 15 ºC (Figure III.3a). Furthermore, a storage temperature × time interaction ($P \leq 0.001$) effect was observed. The apricot C_2H_4 production at 2 ºC remained steady throughout storage with an average C_2H_4 production rate of 0.4 ± 0.3 pmol kg^{-1} s^{-1}. The apricot C_2H_4 production at 15 ºC was higher than that at 2 ºC, with average values of 2.3 ± 1.0 pmol kg^{-1} s^{-1} up to 10 days. Then, a marked increase from day 10 was observed reaching a maximum C_2H_4 production of 7.8 ± 0.8 pmol kg^{-1} s^{-1} after 14 days, followed by a decrease. Thus, apricots stored at 2 ºC did not reach the climacteric stage observed on day 14 in 15 ºC–samples. These findings are in accordance with those previously reported by Christen et al. (2018) and Gouble et al. (2012). Those authors reported a strong storage temperature influence on both climacteric rise and C_2H_4 production of apricot. Christen et al. (2018) and Gouble et al. (2012) established that the lower the storage temperature, the lower the apricot C_2H_4 production rates. Particularly, Christen et al. (2018) reported that 'Goldrich' apricot storage at 8 ºC delayed the apricot climacteric rise compared with 20 ºC–samples, whereas the C_2H_4 production was almost completely inhibited up to 30 days at 1 ºC. In addition, the last authors also observed that the C_2H_4 production and the climacteric rise depend as much on the cultivar as on the fruit maturity stage at harvest.

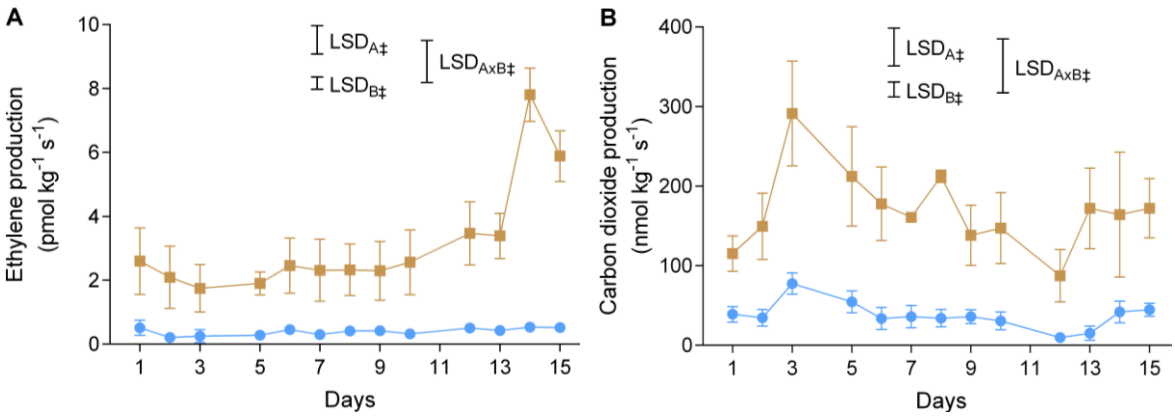


Figure III.3. Ethylene (a) and carbon dioxide production (b) rates of apricot at 2 (●) and 15 (■) ºC (mean (n=5)±standard deviation). The uppercase letters (subscripts) A and B denote time and storage temperature factors, respectively. ‡ significance for $P \leq 0.001$. LSD: Least significant difference (source: Own elaboration).

Based on the low C_2H_4 production, apricot storage at 2 ºC seems to be a good option to decrease the ripening processes triggered by the C_2H_4 production. However, it is well known that 0–10 ºC storage can induce chilling injury and internal breakdown on apricot, and stone

fruit in general, which limits fruit shelf–life to a few weeks (Crisosto et al., 1995). On the contrary, stone fruit storage at temperatures between 15 and 27 ºC allows a normal ripening (compiled by Crisosto et al. (1995). Gouble et al. (2012) found a significant lower C_2H_4 production in two apricot cultivars at 15 ºC regarding 20 ºC storage. Therefore, to allow a normal ripening while C_2H_4 detrimental effects are avoided, C_2H_4 removal techniques such as $KMnO_4$–based scavengers could be used as a complementary tool to storage.

III.3.2.2 Carbon dioxide production

Similar to C_2H_4 production, the apricot CO_2 production was significantly ($P \leq 0.001$) affected by both storage temperature and time factors, and their interaction storage temperature × time (Figure III.3b). The apricot CO_2 production was highly decreased by 2 ºC storage compared with 15 ºC. Nevertheless, a maximum peak was observed on day 3 regardless of the storage temperature, but with different intensity values (77.6 ± 13.5 and 291.2 ± 65.9 nmol kg^{-1} s^{-1} at 2 and 15 ºC, respectively). These findings are in accordance with Gouble et al. (2012), who found higher RR of apricots (cvs. 'Ravicille' and 'Bergeron') at 15 and 20 ºC regarding the stable low RR at 5 and 10 ºC. The peak of CO_2 observed at the beginning of the experiment may have been induced by the airflow rate to which apricots were exposed (Kays & Paull, 2004).

The C_2H_4 and CO_2 production patterns obtained in this experiment suggest that the ripening process of fresh apricot fruit can be delayed at low–temperature storage (2 ºC) by suppressing C_2H_4 production and decreasing CO_2 production. In this sense, although, it has been reported that physiological disorders may occur in most apricot cultivars during refrigerated storage (Crisosto et al., 1995), the storage life of refrigerated apricots could be extended by packaging under MAP conditions (Botondi et al., 2000) or using strategies to avoid C_2H_4 action (Christen et al., 2018; Palou & Crisosto, 2003). Furthermore, as mentioned above, refrigeration needs can be reduced by using C_2H_4 removal techniques, while a normal ripening is allowed.

III.3.3 Gas composition in the modified atmosphere packages

III.3.3.1 Ethylene

The C_2H_4 concentration found within MAP apricots was significantly ($P \leq 0.001$) affected by the $KMnO_4$–based C_2H_4 scavengers used throughout storage at 2 ºC (Figure III.4a). Nevertheless, no significant ($P < 0.05$) C_2H_4 concentration differences were observed between the C_2H_4 scavengers. Moreover, a significant ($P \leq 0.001$) interaction was observed between packaging condition and storage time. Regardless of the packaging condition, the C_2H_4 concentration increased at the beginning of the experiment, reaching the maximum

value on day 3 and then decreasing, remaining almost stable from day 8 until the end of the storage. The maximum C_2H_4 concentration found inside the apricot MAP packages — without C_2H_4 scavengers— was 6.2 nmol L^{-1}, while samples containing C_2H_4 scavengers showed a C_2H_4 concentration lower than 0.3 nmol L^{-1}.

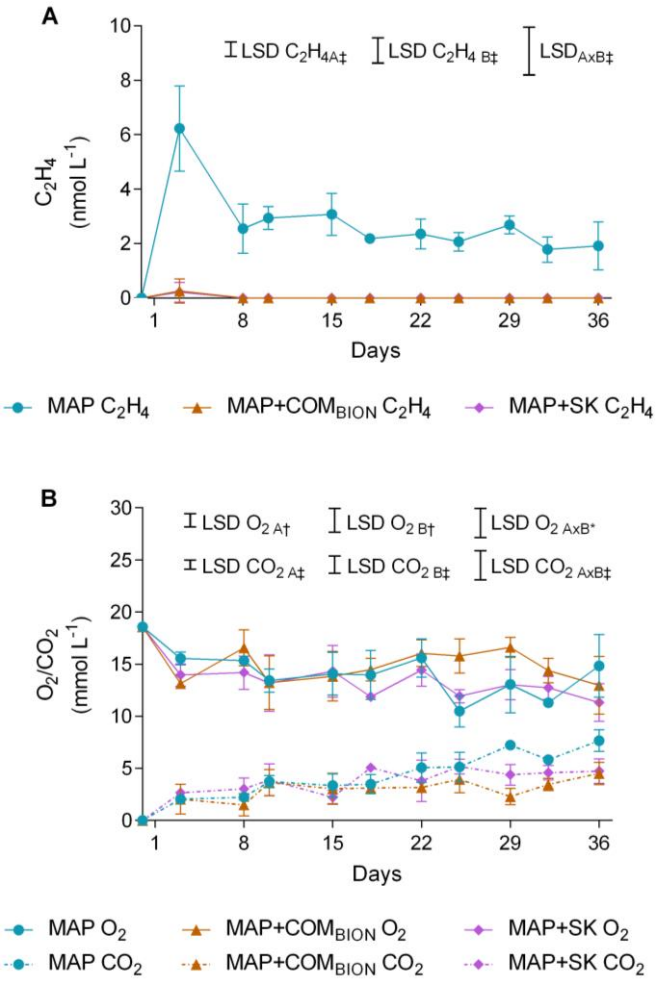


Figure III.4. Gaseous composition (a, C_2H_4; b, O_2/CO_2) in apricot under different packaging conditions (see Table III.1) stored at 2 ºC up to 36 days (mean (n=5)±standard deviation). The uppercase letters (subscripts) A and B denote packaging condition and storage time factors, respectively. *, † and ‡ significance for $P \leq 0.05$, 0.01, and 0.001, respectively. LSD: Least significant difference (source: Own elaboration).

After 8 days at 2 ºC, the C_2H_4 concentration within MAP packages decreased, remaining almost stable until the end of the storage. The observed C_2H_4 concentration pattern is consistent with that previously reported by Pretel et al. (2000), who concluded that the in–package C_2H_4 evolution of apricot fruit is regulated by the interaction between the apricot respiration and the packaging film gas permeability. Moreover, the in-package C_2H_4 concentration was highly decreased at day 8 when the $KMnO_4$–based C_2H_4 scavengers were added into the modified atmosphere packages. Then, C_2H_4 concentration remained

from day 8 at undetectable values until the end of the storage, regardless of the used C_2H_4 scavenger material (Figure III.4a).

Overall, results showed that both the commercial $KMnO_4$–based C_2H_4 scavenger and the developed one can be effectively used as complementary tools to MAP for maintaining low C_2H_4 concentrations inside apricot packages during refrigerated storage. Nonetheless, since 0.5 g of the developed C_2H_4 scavenger and 1 g of the commercial one were used and no difference was observed between the C_2H_4 scavenger patterns, it can be deduced that the same effect can be obtained by using 50 % less amount of the developed C_2H_4 scavenger than the commercial one.

III.3.3.2 Carbon dioxide and oxygen

The CO_2 and O_2 concentrations within the apricot packages were significantly ($P \leq 0.001$ and $P \leq 0.01$, respectively) influenced by the packaging conditions during storage at 2 ºC (Figure III.4b). A strong packaging condition × time interaction was observed for CO_2 ($P \leq 0.001$) at 2 ºC, whereas a lower interaction ($P \leq 0.05$) was found for O_2. The steady-state CO_2 and O_2 concentrations within packages without C_2H_4 scavengers were reached after 10 days at 2 ºC (3.7 ± 0.6 mmol L^{-1} CO_2/ 13.4 ± 1.1 mmol L^{-1} O_2). Nevertheless, the latter behaviour was observed in those packages with C_2H_4 scavengers from day 3 (2.0 ± 1.4 mmol L^{-1} CO_2/ 13.1 ± 0.3 mmol L^{-1} O_2 in the MAP+COM_{BION} packages and 2.7 ± 0.3 mmol L^{-1} CO_2/ 14.0 ± 1.1 mmol L^{-1} O_2 in the MAP+SK ones). The steady-state O_2 and CO_2 concentrations in packages with and without C_2H_4 scavengers were maintained until days 22 and 29, respectively (Figure III.4b). Subsequently, O_2 concentration decreased in MAP and MAP+SK packages at day 25, while the O_2 concentration of MAP+COM_{BION} packages remained stable until day 29. On the contrary, the CO_2 concentration of the MAP packages increased at day 29, remaining almost steady in those apricot packages containing C_2H_4 scavengers during the rest of the storage period. However, higher O_2 concentrations were found in MAP+COM_{BION} packages than in MAP+SK packages after 18, 25 and 29 days of storage, and lower CO_2 concentrations after 18 and 29 days.

As mentioned earlier, low O_2 in–package concentrations (from 1.77 to 2.66 mmol L^{-1}) are usually recommended for apricot storage (Kader, 2002). However, apricots can undergo metabolic disorders when they are exposed to low O_2 concentrations, which can result in sugars>ethanol transformation leading to off-flavour development (Pretel et al., 1999). According to Pretel et al. (2000), apricots should be stored at CO_2 concentrations lower than 6.24 mmol L^{-1} and O_2 concentrations higher than 8.87 mmol L^{-1} to avoid sensory alterations, as well as phytotoxic effects. Then, the equilibrium atmospheres hereby obtained are in agreement with the gas recommended by Pretel et al. (2000). Moreover, the use of C_2H_4

scavengers reduced the time necessary to reach the MAP steady state. Furthermore, the gas composition remained stable for a longer time in the apricot packages containing C_2H_4 scavengers compared with those packages without them. The difference found between MAP+COM_{BION} and MAP+SK packages regarding O_2 and CO_2 concentrations could be attributed to the gas adsorption properties of the materials used as $KMnO_4$ support in each C_2H_4 scavenging product (Álvarez-Hernández et al., 2018). These results agree with previous findings (Álvarez-Hernández et al., 2019), where lower CO_2 concentrations in blueberry packages were obtained when $KMnO_4$–impregnated zeolite sachets were used, regarding packages containing $KMnO_4$–loaded MMT sachets.

III.3.4 Assessment of quality characteristics

III.3.4.1 Weight loss

The apricot weight loss significantly ($P \leq 0.001$) increased during the storage period, being highly ($P \leq 0.001$) influenced by packaging conditions (Table III.3–III.4). Moreover, a significant ($P \leq 0.001$) interaction was observed between packaging condition and storage time during storage at 2 ºC, as well as at 15 ºC. Among the 2 ºC–stored samples, AIR samples showed the highest weight loss rate during storage (an average of 0.7 % weight loss per sampling day), but such weight loss rate was significantly decreased (an average of 0.1 % per sampling day) when samples were stored under MAP. After 36 days at 2 ºC, the average weight loss of MAP samples was noticeably lower than that of AIR samples (0.5 and 3.3 %, respectively). Nonetheless, the apricot weight was maintained stable during storage when $KMnO_4$–based C_2H_4 scavengers were used (Table III.3).

On the other hand, AIR samples showed an average weight loss 2–fold higher than AIR+COM_{BION} and AIR+SK samples at day 8 of 15 ºC (Table III.4). Subsequently, samples containing C_2H_4 scavengers showed a weight loss rate lower than AIR samples until the end of storage. After 20 days of storage at 2 °C, apricots that had been stored with C_2H_4 scavengers showed a 1.4 % weight loss, while a 2.2 % weight loss was found for AIR samples.

Similar to our results, Koyuncu et al. (2010) also observed a reduced weight loss when fresh apricots were kept under MAP during cold storage compared with air conditions. The low weight loss of MAP fruit is related to a low H_2O loss, which in turn is because under MAP technology there is a lower H_2O vapour–pressure deficit than under air storage (Rahman, 2007). Higher CO_2 and lower O_2 concentrations than atmospheric ones may reduce both respiration and C_2H_4 production (Adel A. Kader et al., 1989; Pretel et al., 2000).

Table III.3. Weight loss, firmness, total soluble solids content, titratable acidity, pH, and fungal incidence of apricot under different packaging conditions (see Table III.1) stored at 2 ºC up to 36 days (mean (n=5)±standard deviation) (source: Own elaboration).

Storage time	Packaging	Weight loss (%)	Firmness (N)	SSC (%)	TA (g L^{-1})	pH	SSC/TA	Fungal incidence (%)
Packaging day		-	6.04 ± 0.61	11.1 ± 0.5	14.0 ± 0.9	3.4 ± 0.1	0.8 ± 0.1	-
Day 8	AIR	0.9 ± 0.3	4.81 ± 0.51	10.6 ± 0.2	9.2 ± 0.5	3.6 ± 0.0	1.2 ± 0.0	3.7 ± 6.4
	MAP	0.3 ± 0.0	5.22 ± 0.01	10.7 ± 0.1	9.6 ± 0.9	3.7 ± 0.1	1.1 ± 0.1	0.0 ± 0.0
	MAP+COM_{BION}	0.0 ± 0.0	5.03 ± 0.40	10.4 ± 0.5	11.9 ± 0.4	3.4 ± 0.1	0.9 ± 0.1	0.0 ± 0.0
	MAP+SK	0.0 ± 0.0	5.37 ± 0.41	10.4 ± 0.3	11.7 ± 0.8	3.5 ± 0.1	0.9 ± 0.1	0.0 ± 0.0
Day 15	AIR	1.5 ± 0.5	4.75 ± 0.35	11.0 ± 0.4	9.4 ± 0.3	3.5 ± 0.0	1.2 ± 0.1	3.7 ± 6.4
	MAP	0.3 ± 0.0	5.03 ± 0.27	10.4 ± 0.3	9.7 ± 0.2	3.6 ± 0.1	1.1 ± 0.1	7.4 ± 6.4
	MAP+COM_{BION}	0.1 ± 0.0	4.91 ± 0.47	10.5 ± 0.9	11.4 ± 0.7	3.6 ± 0.1	0.9 ± 0.1	7.4 ± 6.4
	MAP+SK	0.1 ± 0.0	5.02 ± 0.13	10.4 ± 0.6	11.3 ± 0.4	3.6 ± 0.0	0.9 ± 0.1	3.7 ± 6.4
Day 22	AIR	2.3 ± 0.5	4.51 ± 0.39	10.5 ± 0.2	9.8 ± 0.5	3.6 ± 0.0	1.1 ± 0.1	37.0 ± 6.4
	MAP	0.3 ± 0.1	4.96 ± 0.34	9.9 ± 0.6	10.7 ± 0.3	3.6 ± 0.0	0.9 ± 0.1	22.2 ± 11.1
	MAP+COM_{BION}	0.2 ± 0.0	4.91 ± 0.28	10.5 ± 0.5	10.8 ± 0.1	3.6 ± 0.0	1.0 ± 0.0	38.9 ± 5.6
	MAP+SK	0.1 ± 0.1	4.68 ± 0.74	10.6 ± 0.3	9.9 ± 0.1	3.7 ± 0.1	1.1 ± 0.0	11.1 ± 0.0
Day 29	AIR	2.9 ± 0.6	3.44 ± 0.23	11.1 ± 0.4	8.8 ± 0.4	3.9 ± 0.1	1.3 ± 0.0	50.0 ± 5.6
	MAP	0.4 ± 0.1	4.96 ± 0.22	10.6 ± 0.4	9.6 ± 0.9	3.7 ± 0.0	1.1 ± 0.1	40.7 ± 6.4

Table III.3. Continued.

Storage time	Packaging	Weight loss (%)	Firmness (N)	SSC (%)	TA (g L^{-1})	pH	SSC/TA	Fungal incidence (%)
	MAP+COM_{BION}	0.2 ± 0.0	4.86 ± 0.45	10.5 ± 0.4	10.4 ± 0.5	3.8 ± 0.0	1.0 ± 0.1	44.4 ± 11.1
	MAP+SK	0.1 ± 0.1	4.61 ± 0.24	10.3 ± 0.4	9.8 ± 1.3	3.8 ± 0.1	1.1 ± 0.2	37.0 ± 6.4
Day 36	AIR	3.3 ± 0.5	3.42 ± 0.22	10.6 ± 0.2	7.8 ± 0.3	3.9 ± 0.1	1.4 ± 0.1	66.7 ± 11.1
	MAP	0.5 ± 0.1	4.66 ± 0.44	10.7 ± 0.4	9.3 ± 0.9	3.8 ± 0.1	1.2 ± 0.0	48.1 ± 6.4
	MAP+COM_{BION}	0.2 ± 0.0	4.32 ± 0.67	10.8 ± 0.2	9.6 ± 0.9	3.8 ± 0.1	1.1 ± 0.1	44.4 ± 0.0
	MAP+SK	0.2 ± 0.0	4.16 ± 0.34	10.7 ± 0.2	9.7 ± 0.9	3.7 ± 0.0	1.1 ± 0.0	40.7 ± 6.4
Packaging condition (A)		(0.2)‡	(0.51)‡	ns	(0.8)‡	ns	(0.1)‡	(6.9)‡
Storage time (B)		(0.2)‡	(0.62)‡	(0.5)†	(1.0)‡	(0.1)‡	(0.1)‡	(8.5)‡
A×B		(0.5)‡	(0.71)*	ns	(1.2)*	(0.1)*	(0.1)*	(17.0)‡

SSC: Total soluble solids content: TA: Titratable acidity

Values within parentheses represent the least significant difference.

ns, *, †, ‡ significance for $P \leq$ not significant, 0.05, 0.01, and 0.001, respectively.

Table III.4. Weight loss, firmness, total soluble solids content, titratable acidity, pH, and fungal incidence of apricot under different packaging conditions (see Table III.1) stored at 15 ºC up to 20 days (mean (n=5)±standard deviation) (source: Own elaboration).

Storage time	Packaging	Weight loss (%)	Firmness (N)	SSC (%)	TA (g L^{-1})	pH	SSC/TA	Fungal incidence (%)
Packaging day		-	6.04 ± 0.61	11.1 ± 0.5	14. 0 ± 0.9	3.4 ± 0.1	0.8 ± 0.1	-
Day 8	AIR	0.9 ± 0.1	4.28 ± 0.14	10.4 ± 0.4	5.4 ± 0.3	4.1 ± 0.1	1.9 ± 0.1	11.1 ± 11.1
	AIR+COM_{BION}	0.5 ± 0.0	4.77 ± 0.54	10.0 ± 0.3	8.9 ± 0.2	3.6 ± 0.1	1.1 ± 0.1	14.8 ± 6.4
	AIR+SK	0.5 ± 0.1	4.80 ± 0.40	9.7 ± 0.5	9.2 ± 0.7	3.7 ± 0.0	1.1 ± 0.1	14.8 ± 0.0
Day 11	AIR	1.2 ± 0.1	3.82 ± 0.32	9.8 ± 0.4	5.7 ± 0.2	4.2 ± 0.0	1.7 ± 0.0	50.0 ± 5.6
	AIR+COM_{BION}	0.8 ± 0.1	4.12 ± 0.45	10.1 ± 0.2	8.6 ± 0.7	3.9 ± 0.1	1.2 ± 0.1	27.8 ± 5.6
	AIR+SK	0.7 ± 0.1	4.43 ± 0.47	9.1 ± 0.4	9.7 ± 1.0	3.7 ± 0.0	1.0 ± 0.0	22.2 ± 0.0
Day 14	AIR	1.5 ± 0.1	3.69 ± 0.02	10.9 ± 0.3	8.9 ± 0.4	4.4 ± 0.0	1.2 ± 0.1	63.0 ± 6.4
	AIR+COM_{BION}	1.0 ± 0.0	3.72 ± 0.61	11.5 ± 0.2	10.7 ± 0.2	3.8 ± 0.1	1.1 ± 0.0	44.4 ± 11.1
	AIR+SK	0.9 ± 0.1	4.16 ± 0.59	9.9 ± 0.2	10.2 ± 0.6	3.9 ± 0.1	1.0 ± 0.1	44.4 ± 11.1
Day 17	AIR	1.8 ± 0.1	3.63 ± 0.06	10.4 ± 0.2	4.5 ± 0.3	4.5 ± 0.1	2.3 ± 0.1	72.2 ± 5.6
	AIR+COM_{BION}	1.1 ± 0.1	3.72 ± 0.88	9.8 ± 0.5	6.5 ± 0.6	4.0 ± 0.1	1.5 ± 0.2	44.4 ± 0.0
	AIR+SK	1.0 ± 0.1	3.66 ± 0.19	9.9 ± 0.1	7.0 ± 0.7	4.1 ± 0.2	1.4 ± 0.1	50.0 ± 5.6
Day 20	AIR	2.2 ± 0.2	3.59 ± 0.86	9.1 ± 0.1	4.4 ± 0.1	4.5 ± 0.1	2.0 ± 0.1	94.4 ± 5.6
	AIR+COM_{BION}	1.4 ± 0.1	3.44 ± 0.40	9.7 ± 0.5	6.9 ± 0.8	4.2 ± 0.1	1.4 ± 0.1	88.9 ± 0.0

Table III.4. Continued.

Storage time	Packaging	Weight loss (%)	Firmness (N)	SSC (%)	TA (g L^{-1})	pH	SSC/TA	Fungal incidence (%)
	AIR+SK	1.3 ± 0.1	3.65 ± 0.06	9.8 ± 0.5	7.2 ± 0.5	4.1 ± 0.1	1.4 ± 0.0	88.9 ± 0.0
Packaging condition (A)		(0.1)‡	ns	(0.1)‡	(0.7)‡	(0.1)‡	(0.1)‡	(7.8)‡
Storage time (B)		(0.1)‡	(0.85)‡	(0.2)‡	(0.9)‡	(0.2)‡	(0.2)‡	(11.1)‡
A×B		(0.2)‡	ns	(0.3)‡	(1.8)‡	(0.3)‡	(0.3)‡	(19.1)‡

SSC: Soluble solids concentration; TA: Titratable acidity.
Values within parentheses represent the least significant difference.
ns, *, †, ‡ significance for $P \leq$ not significant, 0.05, 0.01, and 0.001, respectively.

Moreover, the two assayed C_2H_4 scavengers reduced apricot weight loss either in combination with MAP at 2 ºC for 36 days or under air conditions at 15 ºC for 20 days. No significant differences were found between the commercial and the developed $KMnO_4$–based C_2H_4 scavengers, regardless of atmosphere conditions and storage temperatures.

The lower H_2O loss with C_2H_4 scavengers might be due to lower cell wall damage. Our results were in agreement with data reported by Ishaq et al. (2009), who found the lowest weight losses in apricots stored using a $KMnO_4$–based scavenger.

III.3.4.2 Fruit firmness

Firmness is one of the main quality attributes that determine the consumer's acceptance of produce. The apricot firmness showed a statistically significant ($P \leq 0.001$) decrease during storage at both 2 ºC and 15 ºC (Table III.3–III.4). Nevertheless, the assayed packaging conditions significantly affected ($P \leq 0.001$) the firmness values of 2 ºC–stored samples, whereas they did not affect AIR samples at 15 ºC ($P > 0.05$). In addition, there was a significant ($P \leq 0.05$) interaction between storage time and packaging condition in 2 ºC–stored fruit, which was not observed at 15 ºC ($P > 0.05$). All samples stored at 2 ºC followed a similar firmness decrease during the first 22 days. Afterwards, an important firmness reduction was observed in AIR samples at 29 days while the remaining samples showed higher firmness (Table III.3). The firmness of AIR samples was decreased by 43.4 % after 36 days at 2 ºC while MAP samples showed a firmness loss lower than 23 %. Fruit firmness remained almost stable under MAP with 5.22-4.66 N from day 8 until the end of the storage period. The firmness of MAP+COM_{BION} and MAP+SK samples did not was significantly affected either between them or when compared with MAP samples. On the other hand, a firmness loss of approximately 3.56 N was found for all the 15 °C–stored apricot samples after the 20–days storage (Table III.4), without differences among packaging conditions.

Results revealed that none of the assayed $KMnO_4$–based C_2H_4 scavengers had a significant effect on apricot firmness neither in combination with MAP at 2 ºC nor in AIR conditions at 15 ºC. Fruit softening is associated with cell wall degradation, which is positively correlated with pectin breakdown into H_2O-soluble pectin and acid-soluble pectin (Fan et al., 2018). The expression of polygalacturonase–related genes was associated with C_2H_4 production and apricot softening, which can be increased by exogenous C_2H_4 exposure (Leida et al., 2011; Palou et al., 2003). Accordingly, Palou & Crisosto (2003) observed an apricot firmness decrease during storage at 5 ºC when $KMnO_4$–based scavengers were used. Li et al. (2018) also reported that fruit softening could be delayed using either 1–MCP or C_2H_4 absorbents at -1.5, 0 and 1.5 ºC. Meanwhile, Christen et al. (2018) and Dong et al. (2002) reported that 1–MCP did not affect apricot firmness during storage at 0, 1 and 8 ºC.

Similarly, our results suggest that apricot softening was not influenced by C_2H_4 removal. The unaffected apricot firmness using C_2H_4 scavengers observed in our study is in accord with Dong et al. (2002) and Fan et al. (2018) who hypothesised that an endogenous C_2H_4 release high enough could trigger the cell wall hydrolysis reducing consequently the fruit softening.

On the other hand, the low firmness loss observed for MAP–stored fruit agrees with the low fruit weight loss registered under MAP conditions. As mentioned in section 3.4.1, it is well known that fruit weight loss is mainly due to respiration, which entails a softening and shrivelling increase. In that sense, Wu et al. (2015) observed that apricot firmness tended to decrease as RR increased. In addition, Pretel et al. (1999) reported a delay in fruit softening under high CO_2 and low O_2 atmospheres. These authors attributed such behaviour to a partial polygalacturonase synthesis inhibition, which results in less soluble pectin and therefore in a lower softening. Then, the observed MAP effect on firmness might be explained by a lower H_2O loss, as well as to lower cell–wall structural changes. Overall, the use of MAP is highly recommended for apricots to delay softening, which is one of the key factors limiting postharvest storage and shelf life of apricots.

III.3.4.3 Soluble solids content, titratable acidity, pH and SSC/TA ratio

Changes in SSC, TA, pH, and SSC/TA ratio of apricot fruit stored under different packaging conditions at 2 and 15 ºC up to 36 and 20 days, respectively, are shown in Tables III.2–III.3. SSC fluctuated throughout storage at 2 and 15 °C, revealing significant decreases ($P \leq 0.01$ at 2 °C and $P \leq 0.001$ at 15 °C). The packaging condition showed a significant effect on the SSC changes only at 15 °C ($P \leq 0.001$). Accordingly, no significant ($P > 0.05$) interaction was found for apricot SSC between storage time and packaging condition at 2 °C, but it was on 15 °C–stored fruit ($P \leq 0.001$). Meanwhile, the TA of apricots gradually tended to decrease at 2 and 15 °C ($P \leq 0.001$) in the function of the storage period and packaging condition. Contrary to TA, apricot pH significantly ($P \leq 0.001$) increased at 2 °C and 15 °C, being affected by the packaging condition only at 15 °C ($P \leq 0.001$). Significant effects were found from the interaction among packaging conditions and storage days for TA and pH of apricots stored at 2 °C ($P \leq 0.001$ and $P \leq 0.05$, respectively), as well as at 15 °C ($P \leq 0.05$ and $P \leq 0.001$, respectively).

There was found a fruit SSC decrease less than 4 % at the end of the storage at 2 °C, regardless of the packaging condition. SSC was better maintained in apricots from MAP+COM_{BION} and MAP+SK samples than in those apricots from MAP, as observed for TA of the 2 °C–stored apricots. This finding agrees with the C_2H_4 patterns followed by such samples, which was above discussed in section 3.3.1. The highest TA decrease was

observed for AIR samples after 8 days at 2 °C followed by MAP samples (31.7 %). Meanwhile, the lowest decrease was observed for both MAP+COM_{BION} and MAP+SK samples (less than 17 %).

The SSC tended to decrease in all samples stored at 15 ° C during the first 11–days storage period, being unaffected by the addition of C_2H_4 scavengers. Nonetheless, the SSC of both AIR and AIR+COM_{BION} samples showed a pronounced SSC increase on day 14, resulting in a mean SSC 1.1– and 1.2–fold higher than that of AIR+SK samples, respectively. Subsequently, the SSC value tended to decrease in AIR and AIR+COM_{BION} samples while remained stable for AIR+SK. The apricot TA decrease was delayed by both the commercial and the developed C_2H_4 scavenger under air conditions at 15 °C.

Results showed that the developed C_2H_4 scavenger significantly controlled the SSC changes of apricots stored at 15 °C. This effect of the developed C_2H_4 scavenger could be explained by means of the molecular–sieve properties of SP —the material used as $KMnO_4$ support for the developed scavenger—, which seems to be able to reach favourable atmospheric conditions for apricot fruit, delaying metabolic activities. The latter finding is consistent with the higher O_2 concentrations and lower CO_2 concentrations found in packages containing the commercial scavenger, compared with packages containing the developed one (Section 3.3). In addition, the apricot TA was highly affected by in–package C_2H_4 concentrations, regardless of the storage temperature. This is in agreement with data reported by Fan et al. (2018), who observed that organic acid degradation can be stimulated by exogenous C_2H_4.

The pH changes were negatively correlated with TA changes. At the beginning of 2 °C storage, the lowest pH values were found for those apricots stored along with C_2H_4 scavengers. As for the 15 °C–stored apricots, the pH increases were strongly reduced when the commercial and the developed $KMnO_4$–based C_2H_4 scavengers were used during air storage, without a significant difference between them. This correspondence confirmed the C_2H_4–dependence of the apricot pH, which was more evident for 15 °C–stored apricots. Furthermore, the lower pH increase rate observed in apricots stored with C_2H_4 scavengers might be explained by a reduction in acid metabolism as was also suggested by the lower TA decrease, resulting in higher retention of acids.

A general SSC decrease/TA decrease trend was observed for apricots from all samples under 2 and 15 °C storage. When a non–starchy fruit is not harvested at the right physiological maturity, they do not increase SSC during ripening, but they decrease in TA (Ishaq et al., 2009; Subedi & Walsh, 2009). The TA decrease results from the organic acid

decomposition into CO_2 and H_2O via glycolysis and tricarboxylic acid cycle (Liu et al., 2019). On the other hand, a decreasing trend of SSC is generally a manifestation of senescence (Fan et al., 2018). However, since apricots are a non–starchy fruit and they were harvested at an early stage, the sugar decrease may be an indicator that the ripening process is going on. The sugar decrease is attributed to the breakdown of soluble sugars into CO_2 and H_2O via respiration (Ali et al., 2015; L. Li et al., 2018).

Crisosto et al. (1998) suggested that the SSC in fresh apricot fruit should be greater than 10 %, while the TA should range from 7 to 10 g L^{-1} (moderate acidity). In this study, the obtained SSC percentages for apricots from all the samples remained close to those percentages recommended by Crisosto et al. (1998) during storage at 2 and 15 °C, being then the acceptable consumer satisfaction determined by the TA content.

In order to reach the highest consumer, a well–balanced content of sugars and organic acids is suggested since the SSC and the TA content are associated with the fruit flavour. The SSC/TA ratio significantly increased for all samples either at 2 or 15 °C. Nevertheless, the apricot SSC/TA ratio increase was significantly delayed by both the commercial C_2H_4 scavenger and the developed one during MAP storage at 2 °C for 36 days, as well as during air storage at 15 °C for 20 days. These findings can be related to the higher SSC/TA ratio found by Fan et al. (2018) in apricots when they were exposed to exogenous C_2H_4, resulting in an accelerated organic acid degradation and therefore in accelerated ripening.

Overall, the metabolic activities can be delayed by removing C_2H_4 with any of the assayed C_2H_4 scavengers during storage at 2 °C (in combination with MAP), as well as at 15 °C (under air conditions).

III.3.4.4 Skin colour

The colour attributes C* and H_{ab}) were significantly affected for all samples by the storage period (Tables III.5 and III.6). The parameter H_{ab} was not affected ($P > 0.05$) by the assayed packaging conditions at 2 ºC, but it was affected ($P \leq 0.05$) by C_2H_4 removal on day 8 at 15 ºC. Both storage time and packaging condition had a significant ($P \leq 0.001$) effect on the skin C* values of 2 ºC–stored apricots, as well as on the C* values of 15 ºC–stored samples. Moreover, there was a significant ($P \leq 0.001$) interaction between storage days and packaging conditions under both assayed storage temperatures.

Apricots showed a skin C* value of 49.6 at processing day. The C* parameter tended to decrease during storage at 2 ºC. The lowest C* changes were found for MAP+COM_{BION} and MAP+SK samples (an average of 0.7 and 0.8 C* units per sampling day, respectively), whereas the highest rate was observed for AIR and MAP samples (1.9 and 1.8 C* units per

sampling day, respectively). The AIR and MAP samples performed a similar fluctuation behaviour throughout storage at 2 ºC, without significant differences between them during the first 29 days. Regarding MAP+COM_{BION} and MAP+SK samples, they were statistically similar during the first 22 days of 2 ºC, but MAP+SK samples showed lower C* values at days 29 and 36.

On the other hand, a similar decrease trend of C* values was observed for all samples stored for 8 days at 15 ºC, regardless of the packaging condition (Table III.6). Subsequently, C* values of AIR samples significantly increased at day 11 and, then kept fluctuating until the end of the storage period. Nevertheless, both AIR+COM_{BION} and AIR+SK samples remained almost stable until the end of storage without significant differences between them.

Overall, the results suggested that the skin colour of apricots was not affected by C_2H_4 removal, since H_{ab} and *L** (Table III.5 and III.6) were not significantly affected throughout storage neither at 2 nor at 15 ºC. This is in agreement with Dong et al. (2002), who noticed that once the apricot ripening process starts, the skin colour change is a C_2H_4–independent process. However, the changes of the colour parameter C*, which points out the colour saturation, were highly controlled by using either the commercial or the developed $KMnO_4$–based C_2H_4 scavenger, regardless of the storage temperature. The C_2H_4 removal was more pronounced at 15 ºC than under AIR conditions. The differences found among packaging conditions after 29 days at 2 ºC could be correlated with the in–package gaseous composition changes observed at this storage time (Figure III.4b). Packages containing the developed scavenger showed lower O_2 concentrations than those samples with the commercial scavenger on day 29. Consistently, Botondi et al. (2000) reported that the atmospheric O_2 concentration had a high influence on the apricot colour.

III.3.5 Fungal incidence

The percentage of apricots with visible mycelial growth increased during storage at 2 and 15 ºC (Tables III.2–III.3), being significantly ($P \leq 0.001$) influenced by both storage time and packaging conditions. Moreover, there was observed a significant ($P \leq 0.001$) interaction between the aforementioned factors. In 2 ºC–stored apricots, significant differences were observed between AIR and MAP samples only after 36 days of storage with 66.7 ± 11.1 and 48.1 ± 6.4 % of infected apricots, respectively.

Table III.5 Skin colour parameters (*L*, a*, b*,* H_{ab} and *C**) of apricot fruit stored at 2 ºC up to 36 days under different packaging conditions (see Table III.1) (mean (n=5)±standard deviation) (source: Own elaboration).

Storage time	Packaging	*L**	*a**	*b**	H_{ab}	C*
Packaging day		57.2 ± 1.1	20.6 ± 1.0	65.4 ± 1.1	65.4 ± 1.3	49.6 ± 0.9
Day 8	AIR	57.2 ± 1.3	21.4 ± 1.2	44.2 ± 0.8	64.1 ± 1.3	49.1 ± 0.9
	MAP	56.2 ± 0.4	21.8 ± 1.2	43.0 ± 0.3	63.1 ± 1.3	48.2 ± 0.7
	$MAP+COM_{BION}$	57.5 ± 2.1	21.6 ± 1.7	43.5 ± 1.5	63.5 ± 2.6	48.6 ± 0.7
	MAP+SK	56.8 ± 0.4	22.7 ± 0.8	44.1 ± 0.4	62.8 ± 1.0	49.6 ± 0.1
Day 15	AIR	57.5 ± 0.5	24.6 ± 2.9	44.8 ± 0.8	61.3 ± 3.3	51.2 ± 0.8
	MAP	57.5 ± 0.8	23.2 ± 0.9	44.6 ± 1.3	62.5 ± 1.5	50.3 ± 0.9
	$MAP+COM_{BION}$	56.5 ± 0.9	22.8 ± 1.7	43.4 ± 0.8	62.3 ± 1.8	49.1 ± 1.1
	MAP+SK	55.7 ± 1.3	22.1 ± 0.5	42.2 ± 1.1	62.3 ± 0.9	47.6 ± 1.0
Day 22	AIR	57.0 ± 0.1	23.5 ± 0.3	41.8 ± 1.0	60.6 ± 0.5	47.9 ± 0.9
	MAP	56.5 ± 0.4	23.1 ± 0.6	42.2 ± 0.5	61.3 ± 0.9	48.1 ± 0.3
	$MAP+COM_{BION}$	56.1 ± 0.5	23.4 ± 0.5	42.1 ± 0.5	60.9 ± 0.3	48.2 ± 0.7
	MAP+SK	55.6 ± 1.1	23.7 ± 1.0	40.4 ± 0.9	59.6 ± 1.1	46.8 ± 1.0
Day 29	AIR	55.7 ± 0.7	24.3 ± 0.9	39.9 ± 1.0	58.7 ± 0.4	46.8 ± 1.3
	MAP	57.9 ± 0.5	21.8 ± 0.3	41.3 ± 1.2	62.1 ± 0.5	46.7 ± 1.1
	$MAP+COM_{BION}$	57.5 ± 2.0	22.5 ± 1.6	42.7 ± 1.0	62.2 ± 2.2	48.3 ± 0.2

Table III.5. Continued.

Storage time	Packaging	*L**	*a**	*b**	H_{ab}	C*
	MAP+SK	57.8 ± 0.2	21.5 ± 0.6	41.3 ± 0.6	62.5 ± 0.8	46.5 ± 0.6
Day 36	AIR	55.8 ± 0.3	23.9 ± 1.3	43.4 ± 1.0	61.2 ± 1.9	49.5 ± 0.3
	MAP	57.4 ± 0.8	23.3 ± 0.4	42.4 ± 0.3	61.2 ± 0.4	48.4 ± 0.4
	$MAP+COM_{BION}$	56.8 ± 1.7	22.7 ± 1.7	41.5 ± 1.3	61.3 ± 2.5	47.4 ± 0.5
	MAP+SK	55.9 ± 0.8	23.6 ± 1.0	38.9 ± 0.8	58.8 ± 1.6	45.5 ± 0.1
Packaging condition (A)		ns	ns	(1.1)‡	ns	(0.9)‡
Storage time (B)		ns	(1.7)‡	(1.4)‡	(2.2)‡	(1.1)‡
A×B		ns	ns	(2.7)‡	ns	(2.3)‡

Values within parentheses represent the least significant difference.
ns and ‡ significance for $P \leq$ not significant and 0.001, respectively.

Table III.6. Skin colour parameters (*L**, *a**, *b**, H_{ab} and *C**) of apricot fruit stored at 15 ºC up to 20 days under different packaging conditions (see Table III.1) (mean (n=5)±standard deviation) (source: Own elaboration).

Storage time	Packaging	*L**	*a**	*b**	H_{ab}	C*
Packaging day		57.2 ± 1.1	20.6 ± 1.0	45.1 ± 1.1	65.4 ± 1.3	49.6 ± 0.9
Day 8	AIR	56.4 ± 1.6	25.7 ± 1.8	41.1 ± 0.0	58.0 ± 1.8	48.4 ± 1.0
	$AIR+COM_{BION}$	58.3 ± 0.9	21.7 ± 1.2	42.3 ± 0.8	62.8 ± 1.0	47.6 ± 1.1
	AIR+SK	58.3 + 0.2	22.0 ± 1.4	41.1 ± 1.3	61.8 ± 0.7	46.6 ± 1.8

Table III.6. Continued.

Storage time	Packaging	*L**	*a**	*b**	H_{ab}	C*
Day 11	AIR	55.8 ± 0.6	26.3 ± 0.9	43.4 ± 0.1	58.8 ± 0.8	50.7 ± 0.5
	AIR+COM_{BION}	57.4 ± 0.3	24.6 ± 0.0	41.6 ± 0.3	59.4 ± 0.2	48.3 ± 0.3
	AIR+SK	57.8 ± 0.9	23.6 ± 0.1	41.1 ± 0.9	60.1 ± 0.7	47.4 ± 0.8
Day 14	AIR	54.8 ± 1.6	26.2 ± 0.3	42.0 ± 0.2	58.1 ± 0.2	49.5 ± 0.3
	AIR+COM_{BION}	55.7 ± 1.3	25.7 ± 1.2	40.4 ± 1.3	57.5 ± 2.1	47.9 ± 0.5
	AIR+SK	56.3 ± 2.2	25.0 ± 0.9	41.0 ± 1.0	58.6 ± 0.3	48.0 ± 1.3
Day 17	AIR	54.6 ± 1.9	26.9 ± 0.6	43.5 ± 0.2	58.3 ± 0.6	51.2 ± 0.4
	AIR+COM_{BION}	54.9 ± 0.6	25.2 ± 0.4	38.4 ± 0.5	56.7 ± 0.6	46.0 ± 0.4
	AIR+SK	55.2 ± 1.2	25.5 ± 1.3	39.9 ± 0.8	57.4 ± 1.0	47.4 ± 1.2
Day 20	AIR	53.3 ± 1.7	26.7 ± 1.0	39.8 ± 0.8	56.1 ± 1.3	47.9 ± 0.6
	AIR+COM_{BION}	54.7 ± 0.4	25.3 ± 1.0	39.9 ± 0.6	57.6 ± 0.6	47.3 ± 1.1
	AIR+SK	55.7 ± 1.1	25.6 ± 1.3	40.8 ± 1.2	57.9 ± 2.0	48.2 ± 0.3
Packaging condition (A)		(1.1)†	(1.2)‡	(1.0)‡	(0.8)*	(1.1)‡
Storage time (B)		(2.1)‡	(1.7)‡	(1.4)‡	(1.9)‡	(1.5)‡
A×B		ns	ns	(2.5)‡	(2.5)†	(2.6)‡

Values within parentheses represent the least significant difference; ns, *, † and ‡ significance for $P \leq$ not significant, 0.05, 0.01 and 0.001, respectively.

Regarding the MAP effect, it was not affected by using $KMnO_4$–based C_2H_4 scavengers throughout storage. However, MAP+SK samples showed lower fungal incidence rates than AIR samples from day 22 until the end of storage with values of 45 and 70 %, respectively.

As expected, apricots showed a high fungal development during 15 ºC storage with values ranging from 89 to 94 % on day 20. Nonetheless, the fungal incidence was effectively controlled by $KMnO_4$–based C_2H_4 scavengers from day 11 to 17. The percentage of infected AIR apricots was 72.2 % after 17 days at 15 ºC, while AIR+COM_{BION} and AIR+SK samples showed fungal incidence rates of 44.4 and 50 %, respectively, at that storage time. A similar effect was obtained by using either the commercial or the developed C_2H_4 scavenger throughout the storage period at 15 ºC.

Postharvest diseases and physiological disorders are the main factors that influence the postharvest losses of stone fruits (Muzzaffar et al., 2018). Many studies have shown that C_2H_4 affects the development of postharvest diseases due to fungal growth in different ways and by different pathways depending on the host-pathogen system (data compiled by Palou et al. (2003). In this study, the fungal incidence was controlled up to 36 days in the 2 ºC–stored apricots utilizing MAP along with the developed $KMnO_4$–based C_2H_4 scavenger. In a similar study performed on apricots inoculated with *Monilinia fructicola*, brown rot development was not influenced by using $KMnO_4$ sachets during storage at 5 ºC (Palou & Crisosto, 2003). The decreased fungal incidence found on apricots from MAP+SK samples could be attributed to the in-package composition promoted by the developed C_2H_4 scavenger (Figure III.4). Besides having an undetectable C_2H_4 concentration, MAP+SK packages showed significantly lower O_2 concentrations than MAP+COM_{BION} packages at days 18, 25 and 29, and higher CO_2 concentrations on day 18 and 29. Furthermore, results suggest that the fungal incidence rate could be significantly decreased by C_2H_4 removal during air storage at 15 ºC, being controlled by the two studied $KMnO_4$–based C_2H_4 scavengers for 17 days.

III.3.6 Sensory evaluation

Sensory evaluations of apricots stored at 2 ºC revealed that MAP+SK samples maintained an excellent sensory quality within the first 15 days of storage (Figure III.5). Meanwhile, overall acceptance, flavour and mouthfeel texture were already perceived as moderately good in the rest of the samples after 15 days (Figure III.5a). Slight off–odour and internal browning were identified in all samples stored at 2 ºC after 29 days, but MAP+SK samples still showed the highest sensory scores (Figure III.5b). Moreover, a visual appearance decrease was observed in all samples after 29 days at 2 ºC, except for MAP+COM_{BION}

samples. The MAP samples showed the lowest sensory scores after the 36 days at 2 ºC, while a good sensory quality was still appreciated in the rest of the samples (Figure III.5c).

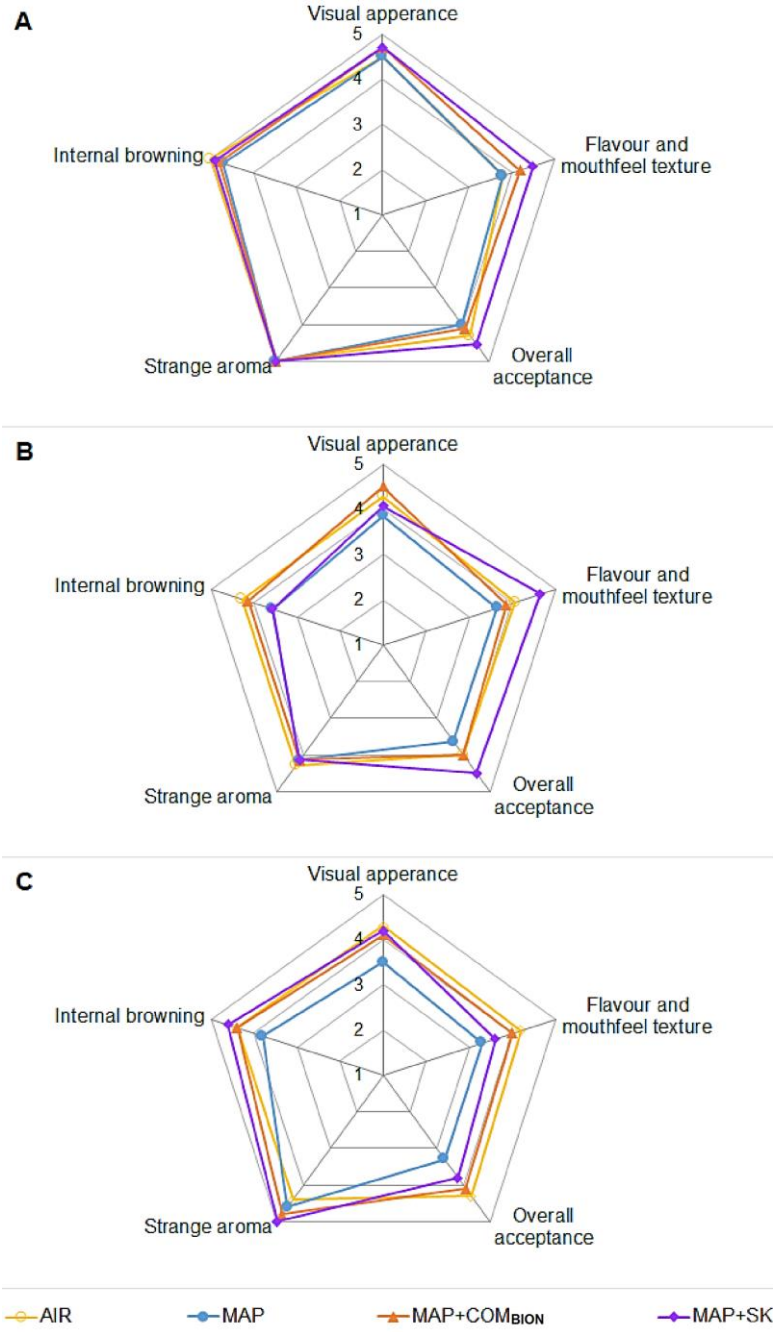


Figure III.5. Sensory quality of fresh apricots stored for 15 (a), 29 (b) and 36 days (c) at 2 ºC under different packaging conditions (see Table III.1) (mean (n=5)) (source: Own elaboration).

The highest sensory scores were scored for AIR+SK samples during the first 14 days of storage, as observed for 15 ºC–stored samples (Figure III.6a–b). A moderately good visual appearance was observed for all samples during the first 17 days of storage, but a slight internal browning was found at day 14 (Figure III.6a–c). Nevertheless, both AIR and AIR+COM_{BION} samples were at the limit of usability at day 11 due to flavour, mouthfeel

texture and overall acceptance scores. AIR+SK samples still showed good sensory quality at 14 days at 15 °C, while AIR+COM_{BION} samples were not sensory accepted due to moderately low flavour and mouthfeel texture scores. After 17 days at 15 ºC, AIR+SK samples showed moderately low flavour and mouthfeel texture scores, as well as a severe internal browning appearance, although a good visual appearance was still appreciated.

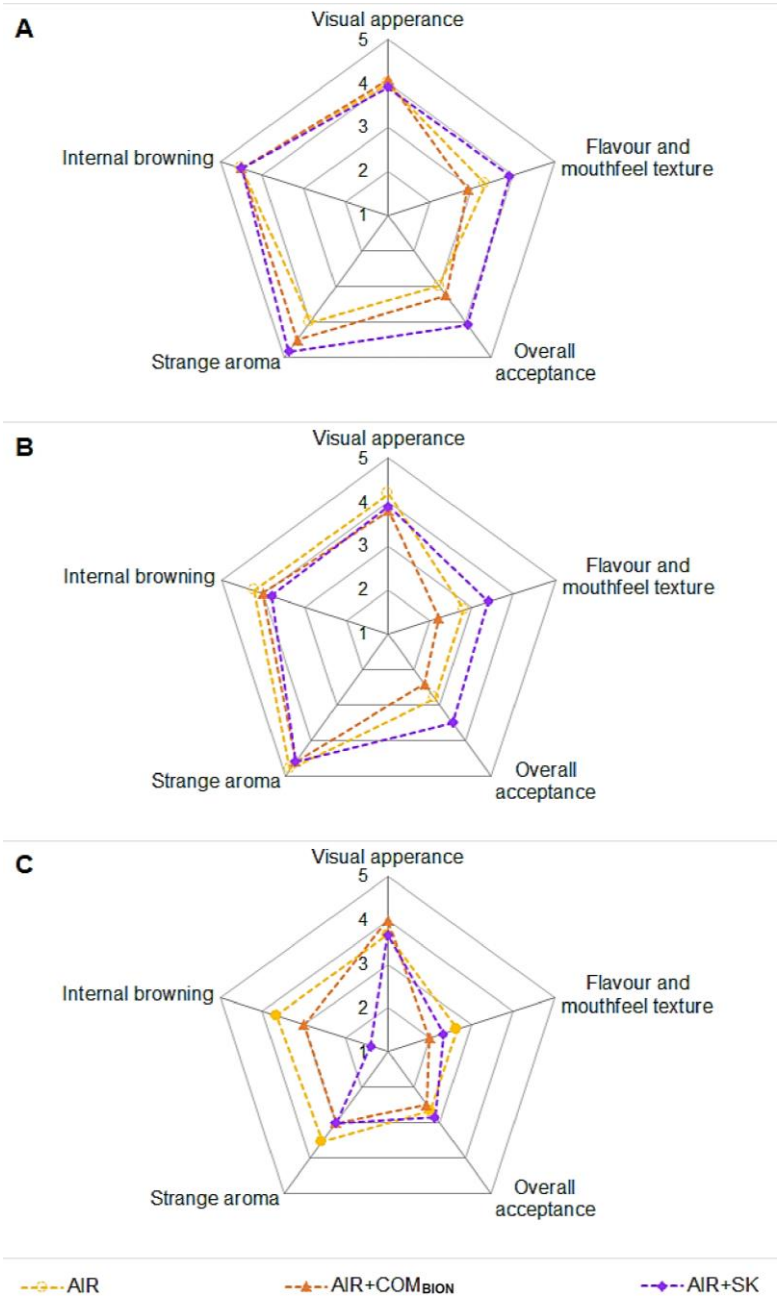


Figure III.6. Sensory quality of fresh apricots stored for 11 (a), 14 (b) and 17 days (c) at 15 ºC under different packaging conditions (see Table III.1) (mean (n=5)) (source: Own elaboration).

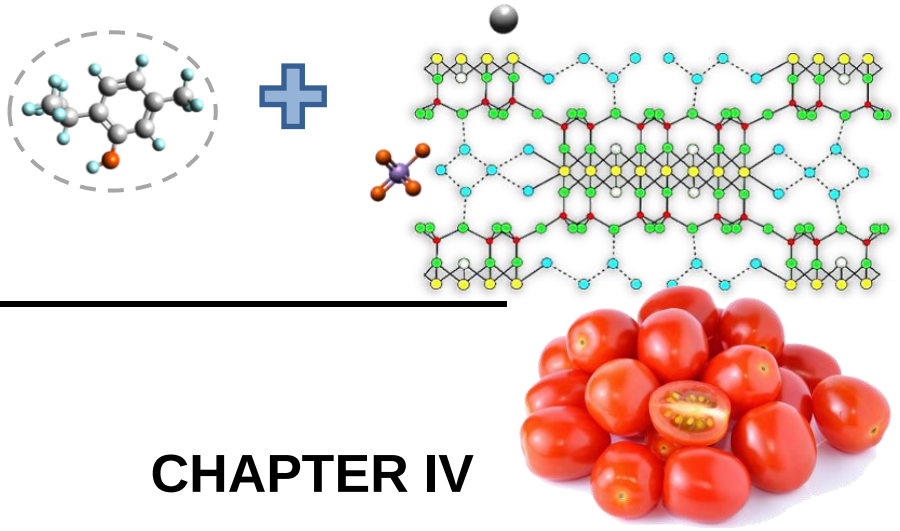
According to sensory scores, flavour and mouthfeel texture were the sensory parameters that highly influenced the sensory overall quality. Therefore, apricots maintained a good sensory quality for 36 days at 2 ºC, regardless of the storage packaging conditions.

Nonetheless, the highest sensory scores were obtained for those samples packaged using the developed C_2H_4 scavenger under MAP conditions. On the other hand, the shelf life of apricots stored under air conditions at 15 ºC could be established in 17 days based on the flavour, mouthfeel texture and overall acceptability scores, although 70 % of AIR samples apricots were infected. Nevertheless, the highest sensory quality was achieved during the first 14 days at 15 ºC using the developed $KMnO_4$–based C_2H_4 scavenger.

Our results agree with those of Crisosto (2006), who found that stone fruit flesh firmness is the main sensory attribute that determines a good eating quality. Moreover, it is accepted that flavour is another important eating quality factor that influences the final consumers' acceptance (Muzzaffar et al., 2018). The fruit flavour is determined by sugar, acid and volatile compound contents. Accordingly, the reduced sensory quality during storage is in agreement with both SCC and TA reductions during apricot storage at 2 and 15 ºC. On the other hand, apricot firmness reduction during storage resulted in a less mouthfeel texture. Overall, flavour changes together with fruit softening resulted in lower overall acceptability as the storage time increased.

III.4 Conclusions of this chapter

Our results showed that the $KMnO_4$–based C_2H_4 scavenging technology helps delay the ripening and senescence processes of fresh apricots, preserving quality for longer by removing C_2H_4 within modified atmosphere packages at 2 ºC or under air conditions at 15 ºC. Nonetheless, the C_2H_4 removal effect was more evident at 15 ºC, when the metabolic processes are faster. Besides, the novel developed C_2H_4 scavenger ($KMnO_4$ supported on SP) provided a more favourable in–package gaseous composition for apricot storage than the commercially used scavenger ($KMnO_4$ supported on zeolite). Furthermore, our findings highlight the importance of the support material in the development of $KMnO_4$–based C_2H_4 scavengers intended to be used in fresh produce packaging systems. In addition, the developed scavenger can be considered as a highly cost-effective postharvest tool since 50 % less quantity was used compared with the commercial scavenger. Nevertheless, there is still the need for an economic study regarding the production costs of this novel scavenger and elucidate the possible limitations of such technology during long storage periods at inadequate not recommended temperatures due to internal browning and softening.



CHAPTER IV

Innovative Active Packaging Combining an Ethylene Scavenger and Encapsulated Essential Oils to Extend the Shelf Life of Cherry Tomatoes

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CHAPTER IV. INNOVATIVE ACTIVE PACKAGING COMBINING AN ETHYLENE SCAVENGER AND ENCAPSULATED ESSENTIAL OILS TO EXTEND THE SHELF LIFE OF CHERRY TOMATOES

IV.1 Introduction

About half of all fruit and vegetables worldwide produced is lost or wasted throughout the food supply chain (Thole et al., 2020). Tomatoes are the most grown and consumed vegetable crop worldwide with approximately 181 million t produced in 2019 (FAO, 2020). Buzby et al. (2016) estimated a fresh tomato waste of approximately 13 % during retail, while this waste has an important economic and environmental impact, together with social concern (Morone et al., 2019). Furthermore, postharvest food losses lead to unnecessary consumption of resources and food insecurity (Morone et al., 2019).

Most of the postharvest losses are related to decay caused by spoilage microorganisms, mainly by plant pathogenic fungi (Deng et al., 2020). Particularly, the decay and quality deterioration of cherry tomatoes is mainly related to grey mould disease (Buendía−Moreno, Ros−Chumillas, et al., 2019). *B. cinerea*, the causative agent of grey mould, is recognized as one of the major phytopathogen affecting more than 200 crop species (AbuQamar et al., 2017). Likewise, contaminated produce may pose a potential consumer's health risk since some plant pathogenic fungi are known to produce mycotoxins (Antunes & Cavaco, 2010). Thus, control of spoilage and pathogenic fungi is critical to reducing postharvest losses while protecting consumers from foodborne diseases.

Antimicrobial active packaging has attracted special attention in the last decade with a special focus on using antimicrobial natural compounds such as plant EOs (Kapetanakou & Skandamis, 2016). Particularly, the monoterpene phenol thymol (5-methyl-2-propan-2-yl-phenol), which is a major component of thyme and oregano EOs, has revealed to be effective against a wide-spectrum of postharvest phytopathogens, including *B. cinerea* (Robledo et al., 2018; Zhang et al., 2019). Thymol is approved as an active substance by the European Commission (Commission Implementing Regulation (EU) 568/2013) and allowed as a food flavouring by the U.S. FDA (21 C.F.R. § 172.515, 2020). However, successful thymol exploitation in active food packaging remains limited due to its highly volatile nature and instability, as well as to the needed of controlling their in-package concentrations to avoid sensory quality alterations (Çakır et al., 2020; Robledo et al., 2018). In addition, phytotoxic effects can appear on horticultural products due to an excessive release of thymol in the packaging atmosphere (López-Reyes et al., 2013).

Encapsulation techniques have been successfully applied for the stabilization, protection and controlled release of active compounds, like EOs, enhancing their availability and thus their efficiency (Deng et al., 2020; Ortiz-Duarte et al., 2019). For this purpose, the chitosan polymer has been preferred as a carrier due to the presence of amino and hydroxyl groups and the polycationicity in its matrix added to its biodegradability, non-toxicity, and biocompatibility with fresh produce (Medina et al., 2019; Ortiz-Duarte et al., 2019). Besides, emitting sachets containing encapsulated volatile antimicrobials integrate an efficient active-packaging system that allows a gradual release of the vapour phase in the packaging headspace (Otoni et al., 2016).

In the last decade, the incorporation of thymol into chitosan-based structures (e.g. coatings and films) has been explored to increase the shelf-life of fresh produce (Medina et al., 2019; Robledo et al., 2018). Nevertheless, there is a limited number of studies concerning thymol-loaded chitosan particles (Çakır et al., 2020). Besides, although some of these studies have shown the *in vitro* effectiveness against some pathogens, they are mainly focused on the characterization of the developed particles, neglecting their antimicrobial activity under *in vivo* conditions (Hu et al., 2009; Wang et al., 2019).

On the other hand, it is well known that C_2H_4 promotes fungal mycelium growth and influences both fungi and plant responses during fungal-plant interactions (Tudzynski & Sharon, 2002). In this sense, C_2H_4 scavenging systems have shown potential to control the fungal rotting of horticultural commodities. One of the most used tools for scrubbing C_2H_4 are those based on $KMnO_4$, a potent oxidizing agent able to break down the C_2H_4 double bond giving rise to CO_2 and H_2O (Álvarez-Hernández et al., 2019). Furthermore, to improve the chemical reactivity of such oxidant, it is usually supported by porous mineral materials (Álvarez-Hernández et al., 2018). In this sense, we have recently developed a $KMnO_4$-loaded SP able to decrease fungal incidence on apricot during storage, while highly preserving the fruit quality (Álvarez-Hernández et al., 2020).

In the present study, we aimed to evaluate the combined effect of thymol (non- or encapsulated within chitosan particles) and an C_2H_4 scavenger, as a sachet-based active packaging, on fungal development and fruit quality preservation during postharvest storage. The antifungal activity was assayed against *B. cinerea* growth at 11 °C both *in vitro and in vivo*. The effect of selected active sachets was evaluated on cherry tomato quality changes up to 28 days at 11 °C + 3 days at 22 °C.

IV.2 Material and methods

IV.2.1 Plant material and chemicals

Cherry tomato (*Lycopersicon esculentum* Mill. 'Dolcetini') was grown in the Southeast of Spain (Agrícola Gaobe S.L., Almería, Spain) under greenhouse conditions according to integrated pest management cultural practices. Cherry tomato fruit was harvested at the turning ripening stage in January during the early morning. Then, cherry tomatoes were transported 180 km by car to the Pilot Plant of the Institute of Plant Biotechnology (Universidad Politécnica de Cartagena), where they were selected (defect-free and similar size and skin colour) and then sorted in a cold room at the studied temperature (11 ºC) during 24 h for thermal equilibrium before the experiment.

All the used microbial media were acquired from Scharlau Chemicals (Barcelona, Spain). Streptomycin sulphate, HCl (37 %) and dichloromethane were purchased from ITW Reagents (Barcelona, Spain). $KMnO_4$, thymol, TPP, Tween 80 and chitosan (low molecular weight (50,000-190,000 Da); 75–85 % degree of deacetylation) were supplied by Sigma–Aldrich (Steinheim am Albuch, Germany). SP (15/30 mesh) was acquired from Bolaseca (Murcia, Spain). Bi–On® R12 (Bioconservacion S.A., Barcelona, Spain) was acquired as a commercial effective $KMnO_4$–based C_2H_4 scavenger due to be one of the most effective in the market (Álvarez-Hernández et al., 2019a).

IV.2.2 *Botrytis cinerea* strain

B. cinerea was isolated from the fruit of *Capsicum annum* L. (Águilas, Murcia, Spain) infected by Botrytis blight (grey mould) and purified in PDA medium as described by Martínez et al. (2007). A series of inoculated PDA plates were incubated at 25 ºC under light/darkness regimen until the fungi began to grow. *B. cinerea* was purified by transferring 7.4–mm diameter agar-mycelium plugs with somatic hyphae from the periphery of the isolated colony to fresh PDA medium. The PDA medium was supplemented with 0.1 g L^{-1} streptomycin sulphate to prevent bacterial growth. The inoculated plates were light- and dark-incubated at 20 °C for 5 days.

IV.2.3 Preparation of thymol-loaded chitosan particles

Thymol was encapsulated in chitosan particles following the emulsification method described by Hosseini et al. (2013). Briefly, chitosan solution (1 % w/v) was prepared by dissolving chitosan flakes in aqueous acetic acid solution (1 % v/v) at 40-50 ºC. The chitosan solution was then centrifuged at 9,000 × g for 30 min. The supernatant was

collected, and vacuum filtrated through a Whatman® Grade 589/2 filter paper. Subsequently, 0.45 g of Tween 80 (HLB 15.9) were added to 40 mL of the filtrated chitosan solution and kept under vigorous mechanical stirring for 2 h at 45 ºC. Next, 4 mL of dichloromethane containing 0.8 g thymol were gradually dropped into the chitosan solution for 10 min. This operation was performed under an ice-bath condition and using continuous homogenization (13,000 rpm; Ultra-Turrax® T18, IKA®-Werke GmbH & Co. KG, Staufen, Germany). Concomitantly to the thymol addition, 40 mL of TPP solution (0.4 % *w/V*) were dropwise added to the obtained emulsion under continuous stirring for 40 min. The formed particles were collected, washed with distilled H_2O by centrifugation (9,000 × g for 30 min, 4 ºC) and freeze-dried at -35 ºC for 72 h. The thymol-loaded chitosan particles were stored in vacuum-sealed bags at 4 ºC until analysis.

IV.2.4 Preparation of potassium permanganate-loaded sepiolite

A $KMnO_4$-based C_2H_4 scavenger supported by an acid-treated SP was prepared as previously described (Álvarez-Hernández et al., 2020). Briefly, SP was washed and purified through an acid treatment with HCl at 80 ºC for 2 h. Subsequently, the acid-treated SP was washed several times with distilled H_2O until the elimination of chloride ions. The final SP slurry was dried at 110 ºC for 14 h and ground in a ball mill. The acid-treated SP was dispersed into hot H_2O (70 ºC) and then impregnated with a saturated $KMnO_4$ solution considering a proportion of 10 g $KMnO_4$ per 100 g of clay. Finally, the resulting $KMnO_4$-loading SP was dried at 60 ºC and ground. The obtained clay powder (hereinafter referred to as SK) was stored in a desiccator at room temperature until use.

IV.2.5 Preparation of active sachets with ethylene scavenging and antimicrobial functions

Active sachets carrying the C_2H_4 scavenger (1 g of SK) and/or thymol (either encapsulated (ET) or non-encapsulated (T); at different dosages) were prepared (Table IV.1). The T doses (0.04, 0.09, 0.19 and 0.38 g) per sachet were selected based on the method previously described by Hosseini et al. (2013) for the preparation of essential oil-loaded chitosan particles. Besides, 0.2, 0.5 and 1 g of chitosan particles containing 0.04, 0.09 and 0.19 g of reagent thymol, respectively (determined by UV-vis spectrophotometry according to Hosseini et al. (2013)), per sachet were selected based on the T performance. Tyvek® film (220 µm thickness; DuPont, Wilmington, DE, USA), a HDPE material, was used to form the sachets due to its high gas permeation with low H_2O vapour permeability (Álvarez-Hernández et al., 2019). According to Table IV.1, the active components were added inside the Tyvek® sachets (6.0 × 6.5 cm), which were then heat-sealed. To prevent a $KMnO_4$-thymol reaction, a H_2O vapour permeable film (composite bilayer film: 12-µm PE

terephthalate + 35-µm PE; Plásticos del Segura, Murcia, Spain) was used to create an internal separation between the active components inside the sachet. Besides, such intermediate layer property was thought to allow migration of H_2O resulting from the $KMnO_4$-C_2H_4 interaction toward the thymol compartment facilitating the thymol vapour release.

Table IV.1. Sample identification and description of active components contained in the treatment sachets (source: Own elaboration).

Nomenclature	Active function	Sachet treatment description
SK	Ethylene scavenging	1 g of $KMnO_4$-loaded sepiolite
0.04T	Antimicrobial activity	0.04 g of thymol reagent
0.09T		0.09 g of thymol reagent
0.19T		0.19 g of thymol reagent
0.38T		0.38 g of thymol reagent
0.57T		0.57 g of thymol reagent
SK+0.04T	Ethylene scavenging + Antimicrobial activity	1 g of $KMnO_4$-loaded sepiolite + 0.04 g of thymol reagent
SK+0.09T		1 g of $KMnO_4$-loaded sepiolite + 0.09 g of thymol reagent
SK+0.19T		1 g of $KMnO_4$-loaded sepiolite + 0.19 g of thymol reagent
SK+0.38T		1 g of $KMnO_4$-loaded sepiolite + 0.38 g of thymol reagent
SK+0.57T		1 g of $KMnO_4$-loaded sepiolite + 0.57 g of thymol reagent
SK+0.04ET	Ethylene scavenging + Antimicrobial activity	1 g of $KMnO_4$-loaded sepiolite + 0.04 g thymol chitosan-based encapsulated
SK+0.09ET		1 g of $KMnO_4$-loaded sepiolite + 0.09 g of g thymol chitosan-based encapsulated
SK+0.19ET		1 g of $KMnO_4$-loaded sepiolite + 0.19 g of g thymol chitosan-based encapsulated

IV.2.6 Ethylene and carbon dioxide production

The C_2H_4 and CO_2 production by cherry tomatoes stored at 11 ºC were determined following the procedure described by Martínez-Hernández et al. (2013). Five cherry tomato samples (165.9 ± 8.8 g) with similarity in size and free from any damage were placed into 1–L glass jars. The jars were closed with a rubber stopper and subjected to a humidified airflow at 20 mL min^{-1} to avoid alteration of metabolic respiration processes. To ensure a stabilized fruit metabolism, cherry tomato samples were allowed to acclimate for 15 h at the setup test conditions. After that, C_2H_4 and CO_2 fruit production were daily quantified (up to 20 days) by gas chromatography (7820A GC System; Agilent Technologies, Santa Clara CA, USA) as described in Álvarez-Hernández et al. (2019).

For measurements, the jars were hermetically sealed for 1 h, and then a 1-mL headspace gas was collected and injected into the GC system. After taking the air samples, the jars were reconnected to the airflow. Gas calibration was done by comparison with an external $CO_2/O_2/C_2H_4$ mixture (gas molar fraction 10 % / 10 % / 10 ppm) standard (Praxair, Molina de Segura, Spain). The production of C_2H_4 and CO_2 was expressed as pmol kg^{-1} s^{-1} and nmol kg^{-1} s^{-1}, respectively.

IV.2.7 Antifungal evaluations

IV.2.7.1 *In vitro* effect of the prepared sachet-based systems on mycelial growth of *Botrytis cinerea*

Aseptically, agar-mycelium fragments (2.2 ± 0.4 cm^2) were extracted from the growing edge of the 5-days-old *B. cinerea* culture and placed at the centre of fresh streptomycin-containing PDA plates (90-mm diameter). Four plates per treatment (Table IV.1) were inoculated. Inoculated plates were separated into pairs and placed within 1–L PP trays. To provide the in-package atmosphere with H_2O vapour and C_2H_4 naturally generated by fruit metabolism, 10 fresh and sanitized tomatoes were previously placed into each tray. The trays were heat-sealed with a 35-µm oriented PP film containing inside a sachet attached to the centre, as mentioned above. Inoculated plates packaged in the absence of an active sachet were used as controls. The film sealed trays were cut across on one side of the lidding films and then light-incubated at 11 °C. Bioassays ended when the fungal mycelium in any of the control plates was close to the Petri dish wall.

Mycelial growth was analysed through surface area measurements using the ImageJ software (NIH, Bethesda, MD, USA) as described in Martínez et al. (2007). The surface area (cm^2) was daily measured from the edge of the initial inoculum to the perimeter of the

colonies. The fungal development was characterized as colony extension by the growth rate (cm^2 $days^{-1}$), defined as the variation of the surface covered during a considered time. The growth inhibition (%) by the different treatment sachets was determined from the percentage difference between the area of the fungus growing in control plates and the area of each colony incubated with a sachet at the same time.

IV.2.7.2 Efficacy of the prepared sachet-based systems to control grey mould infection on cherry tomatoes

For the pathogenicity test, *B. cinerea* conidia were scraped from culture media and suspended in sterile distilled H_2O and then, counted using a standard haemocytometer.

In a disinfected cold room at 8 ºC, whole cherry tomatoes were sanitized by immersing them in a NaClO solution (100 mg L^{-1}; adjusted to pH 6.5 with acid citric) for 2 min, rinsed with tap H_2O for 1 min and then drained and air-dried on filter paper. Sanitised cherry tomatoes were individually supported on sterilized 33-mm PE flat-top caps, which were previously placed inside 1–L PP trays (10 units per tray). After that, each fruit was wounded (2-mm long and 1-mm deep) using a sterile scalpel and inoculated with a 5 µL drop of the *B. cinerea* conidia suspension (2.6×10^5 conidia mL^{-1}). Then, the trays were heat-sealed with a 35-µm oriented PP lidding film containing a treatment sachet attached to the inner side at a centred position. The applied treatments are shown in Table IV.1. Inoculated cherry tomatoes packed without treatment sachet were used as controls. The top lidding films were cut across on one side to allow environmental atmospheric conditions, as well as to facilitate subsequent monitoring of decay. The packages were kept for 26 days under the same storage conditions described above. The experiment was conducted using 3 replicates per each treatment (i.e. 3 trays per treatment). The incidence and severity of decay were evaluated in each tray according to Martínez & González (2013) through the DI using the following equation:

$$DI = \frac{(P_1 \times 0)+(P_2 \times 1)+(P_3 \times 2)+(P_4 \times 3)}{TF} \quad (25)$$

where P_1 is the number of fruit without decay, P_2 is the number of fruit decayed without mycelium, P_3 is the number of fruit decayed with white mycelium, P_4 is the number of fruit decayed with grey mycelium, and TF is the total number of cherry tomatoes.

IV.2.8 Effect of active sachets on cherry tomato quality during postharvest shelf life

The packaging process was carried out in a disinfected cold room at 8 ºC. Healthy cherry tomatoes (10 units: 176.5 ± 21.43 g) were packed in 1–L rigid PP trays thermo-sealed on

the rim with an oriented PP film (35 µm thickness; Plásticos del Segura, Murcia, Spain). Before sealing, one treatment sachet (active sachet) was fixed to the centre inside covering films with double-sided tape as is schematically illustrated in Álvarez-Hernández et al. (2019). The following three treatments were applied: 1 g of the commercial C_2H_4 scavenger Bi–On® R12 (Bioconservacion S.A., Barcelona, Spain), which is made of $KMnO_4$ supported onto zeolite granules in cylindrical pellet form (COM), 1 g of the prepared $KMnO_4$-loaded SP (SK), and 1 g of the $KMnO_4$-loaded SP plus 0.04 g of ET (SK+0.04ET). Cherry tomatoes packed without active sachet were used as control (CTRL). To allow environmental atmospheric conditions, 10 holes of 800-µm Ø were made on the tray lidding films. The fruit packages were kept for 28 days at 11 °C under continuous light and 90–95 % RH in a 27.47–m^3 cold room (2.70 x 3.70 x 2.75 m) equipped with an air–cooling system (Tecnidex, Valencia, Spain). Physicochemical and sensory quality determinations were performed on 3 random fruit packages (i.e. 3 replicates) per treatment on days 0 (packing day), 7, 13, 21, and 28 days, and after 3 additional days at 22 °C (44 ± 7 % RH) to simulate retail holding conditions. The cherry tomato samples to be analysed were left to acclimate at room temperature for 1 h before quality measurements.

IV.2.8.1 Physicochemical analyses in cherry tomato fruit

Cherry tomato weight loss was monitored throughout storage using an analytical balance (Ohaus EX124; Parsippany, New Jersey, USA). The same samples were used at each sampling time during the 28-days storage. The fruit weight loss was expressed as the percentage difference between the initial and the current net weight at each sampling day.

Fruit firmness and skin colour were determined on 5 randomly selected cherry tomatoes per tray. A compression test was performed on the equatorial region of each whole fruit using a texture analyser (LFRA–4500; Brookfield AMETEK; Middleboro, MA, USA) equipped with a 25.4–mm diameter cylindrical acrylic probe. Results were expressed in Newtons (N). Skin colour was determined in terms of CIE *L*a*b** colour scale using a CIE Standard Illuminant/viewing angle D65/2°. Measurements were performed on 3 different skin points of each fruit through a colourimeter (Chroma Meter CM–A131, Minolta; Tokyo, Japan) with an 8–mm measuring aperture. Before measurements, the colourimeter was calibrated with a white reference plate. The colour value was presented as the CI *a*/b** and the COL presented in Equation 2, according to be the recommended reference indices for tomato quality (as reviewed by Pathare et al. (2013)).

$$COL = (2{,}000 \times a^*)(L^* \times C^*) \quad (26)$$

The SSC, pH and TA determinations were performed as reported by Martínez-Hernández et al. (2019). A juice sample was obtained from 5 randomly selected cherry tomatoes per tray using a blender machine (MX2050 blender, Braun, Germany). The SSC of the juice samples was determined with a digital handheld refractometer (Atago N1; Tokyo, Kanto, Japan) at 20 ºC and expressed as % (sugar equivalents in g 100 g^{-1}). The pH was measured using a pH−meter (Basic20, Crison; Alella, Cataluña, Spain). The TA of diluted juice (5 mL juice plus 45 mL distilled H_2O) was performed employing an automatic titrator (T50, Metter Toledo; Milan, Italy) with 0.1 M NaOH to pH 8.1 and expressed as citric acid equivalents in g L^{-1}.

IV.2.8.2 Sensory evaluation in cherry tomato fruit

Sensory analyses were performed according to international standards (ASTM, 1986) by 10 trained assessors aged 22-72 years (5 women and 5 men). Sensory tests were conducted in a standard room (ISO_8586:2012; ISO (2012)) equipped with individual tasting booths. Colour, flavour, mouthfeel texture and overall acceptability were evaluated using a hedonic scale ranging from 5 to 1 (5: extremely good; 3: fair, LU; 1: extremely bad). Furthermore, a 5–point rating scale of damage incidence and severity (5: none; 3: moderate; 1: severe) was used for fruit dehydration/ skin shrivel.

IV.2.8.3 Sensory evaluation in cherry tomato fruit

To describe tomato quality changes mathematically, the time-dependent quality attributes were fitted with zero- and first-order kinetics as well as with the Weibull model using the Origin® 8.6 (v. 86E; OriginLab Corporation, Northampton, MA, USA) software. The curve fitting was performed with a 95 % confidence level. As reported by Amodio et al. (2013), the cumulative Weibull distribution function may be written as:

$$C_t = C_0 exp[-(\frac{t}{\alpha})^{\beta}] \quad (27)$$

Where Ct is the value of the quality attribute at time t, C_0 is the initial quality of the cherry tomato, k is the rate constant or quality degradation coefficient, and t is the storage time (day). In the Weibull model, α is the scale factor (in days), and β is the shape factor (dimensionless). The reciprocal of scale factor 1/α was considered as the Weibull model's rate constant.

Meanwhile, zero- and first-order kinetic models are given by Equation 21 and 22, respectively.

$$C_t = C_0 - k \times t \quad (28)$$

$$C_t = C_0 \times e^{-k \times t} \quad (29)$$

The goodness of model fit was evaluated by the adj. R^2, the SSE, and the RMSE.

IV.2.9 Statistical analysis

The experiments were conducted in a randomized factorial design. Four *B. cinerea*-inoculated plates per treatment were used for the *in vitro* experiment. Three replicates per treatment and 10 fruit units per replication were used for both the pathogenicity test and fruit quality determinations during cool storage and after shelf-life periods. A two-way ANOVA was performed for each studied parameter, at each storage condition, using SPSS software (v.19 IBM, Armonk, NY, USA). Mean separations were conducted by the Tukey's multiple range test ($P \leq 0.05$).

IV.3 Results and discussion

IV.3.1 Ethylene and carbon dioxide production of tomato cherry fruit

The cherry tomato RR fluctuated throughout the evaluation time at 11 °C, staying between 45 and 85 nmol kg^{-1} s^{-1} during the first 16 days. A maximum RR of 97.9 ± 2.5 nmol kg^{-1} s^{-1} was observed on day 18 (Figure IV.1A). The C_2H_4 production rates of cherry tomato showed the same behaviour as RR. The cherry tomato fruit did not show marked C_2H_4 production rate variations from the second day of evaluation, although it showed the highest C_2H_4 production rate (10.1 ± 0.9 pmol kg^{-1} s^{-1}) on day 1 (Figure IV.1B). The observed initial C_2H_4 production rate declined to 6.5 ± 0.5 pmol kg^{-1} s^{-1} after 2 days and then it remained practically steady until the end-point storage with an average C_2H_4 production rate of 4.3 a 1.4 pmol kg^{-1} s^{-1}.

The observed RR behaviour was in agreement with that previously reported in cherry tomato at 8 and 25 °C (Manasa et al., 2018; Wang et al., 2017). Furthermore, a similar RR was also found in Roma-type tomato at 20 °C (Lee et al., 2007) and tomato cv. Daphne F1 at 11 °C (Tzortzakis et al., 2019). On the other hand, the reported C_2H_4 production rates are 10-12.5 pmol C_2H_4 kg^{-1} s^{-1} at 10 °C (Suslow & Cantwell, 2002), which agrees with our results. Moreover, our results agreed with those of Islam et al. (2012) and Taye et al. (2019), who found a high initial C_2H_4 production rate in 'Unicorn' cherry tomato at 5, 10, 11 and 25 °C, followed by a pronounced decrease and then a steady-state at low production rate.

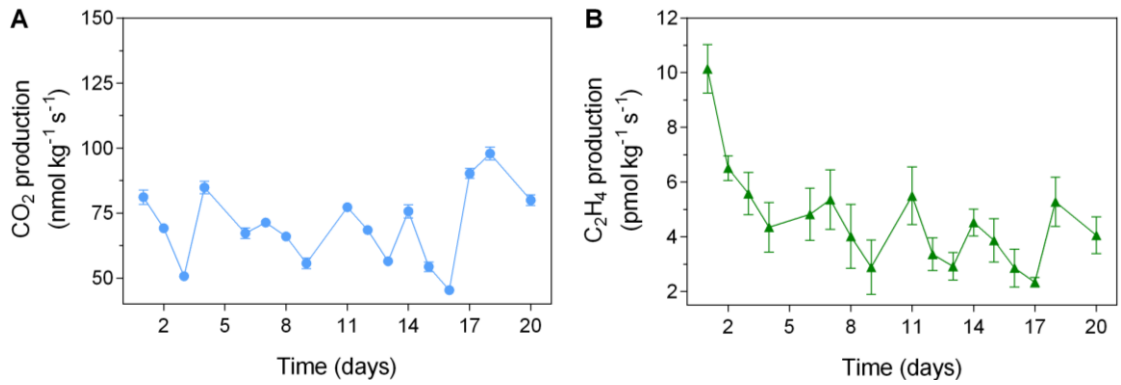

Figure IV.1. Respiration (A) and ethylene production (B) rates of cherry tomato fruit at 11 °C (mean (n=5)±standard deviation) (source: Own elaboration).

Such high initial C_2H_4 production rate may be explained by an abiotic stress response of the fruit to the implemented postharvest storage conditions (mainly due to the airflow rate to which tomatoes were exposed (Kays & Paull, 2004)), being subsequently downregulated when the plant cell metabolism was adapted to that conditions (Barbosa et al., 2011).

Although the reported cherry tomato C_2H_4 production rates are typically low, in–package C_2H_4 removal is a postharvest key technique since trace C_2H_4 concentrations can stimulate fungal decay (Zhang et al., 2017). In this sense, Taye et al. (2019) recently reported that using C_2H_4 control treatments leads to better quality and storability of cherry tomato compared with untreated fruit.

IV.3.2 Antifungal evaluations

IV.3.2.1 In vitro antifungal activity of the prepared sachet-based systems on mycelial growth and development of *Botrytis cinerea*

B. cinerea mycelium grew during incubation time, highly affecting the sachet presence to its growth (Figure IV.1). Furthermore, both treatment sachet and incubation time interaction were significant ($P \leq 0.001$). Overall, no increase in the colony area was observed during the first two days of incubation (Figure IV.1A). Indeed, CTRL samples (Figure IV.1B) typically shown a microbial growth curve consisting of a lag phase (≈day 2), an exponential phase (days 3-5) and then, the beginning of the stationary phase (≥ day 6). In comparison with CTRL plates, the SK sachet slightly controlled mycelial area development after 5 days-incubation (Figure IV.3). Meanwhile, T-carrying sachets completely inhibited mycelial growth through incubation time, regardless of thymol reagent dose. No added benefit was observed when the SK agent was included in the T-carrying sachets.

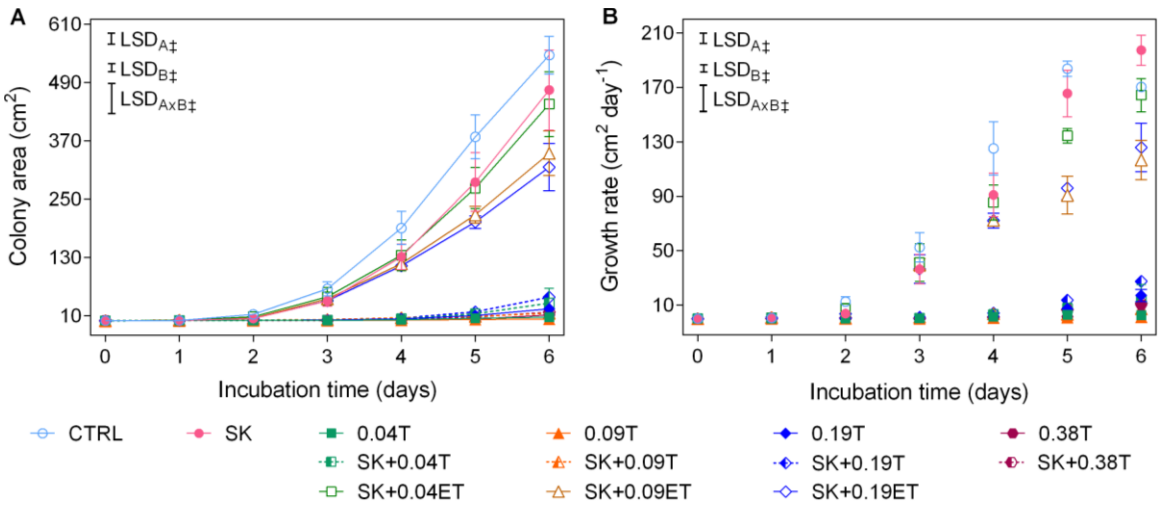

Figure IV.2. Mycelial growth (A) and growth rates (B), as a function of variation in colony area with time, of *Botrytis cinerea* on potato dextrose agar plates at 11 °C up to 6 days under different packaging systems (see Table IV.1) (mean (n=5)±standard deviation). Each point represents the average of 4 colonies and vertical lines are the standard deviation. The uppercase letters (subscripts) A and B denote the packaging system and incubation time factors, respectively. ‡ significance for $P \leq 0.001$. LSD: Least significant difference (source: Own elaboration).

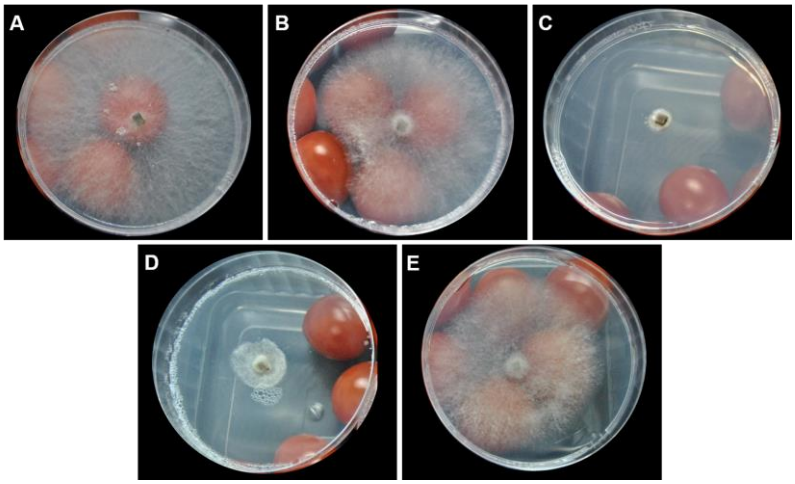

Figure IV.3. Mycelia of *Botrytis cinerea* growing on potato dextrose agar plates after 7 days at 11 °C in the absence of a treatment sachet (A) and under SK ($KMnO_4$-loaded sepiolite; B), 0.04T (0.04 g thymol; C), SK+0.04T ($KMnO_4$-loaded sepiolite and (0.04 g thymol; D) and SK+0.04ET ($KMnO_4$-loaded sepiolite and encapsulated 0.04-g thymol; E) sachets (source: Own elaboration).

On the other hand, SK+0.04ET, SK+0.09ET and SK+0.19ET sachets revealed a fungal growth inhibition of approximately 19, 37 and 42 %, respectively, as compared with CTRL samples. Thymol encapsulation in chitosan allowed a controlled release of this antimicrobial compound since lower thymol concentrations were probably achieved, as deducted from the higher *B. cinerea* growth under ET, as compared with T-containing samples (Figure IV.3). In agreement, the polycationic character of chitosan facilitates the trapping of active agents and their slow release (Ortiz-Duarte et al., 2019).

Overall, T-carrying sachets exhibited the highest fungal inhibition (≥ 91 %), which is related to the membrane disruption and distortion of *B. cinerea* hyphae, and cell components leakage (Zhang et al., 2019). Nevertheless, off-flavours may be perceived in food products due to an initial high concentration of thymol, probably released from sachets to the packaging atmosphere. In this sense, Viacava et al. (2018) studied the effect of microencapsulated and non-encapsulated thyme EOs on organoleptic characteristics of minimally processed lettuce. The latter authors found that all tested non-encapsulated thyme essential oil concentrations negatively affected the colour, texture and odour acceptance. Meanwhile, thyme essential oil microencapsulation was helpful to minimize its negative impact on sensory attributes of lettuce, being the lowest concentration of encapsulated essential oil the most effective in maintaining a good sensory quality.

IV.3.2.2 Efficacy of the prepared sachet-based systems to control grey mould infection on cherry tomatoes

The DI of *B. cinerea*-infected cherry tomatoes tended to increase throughout the storage period in a treatment sachet-dependent manner (Figure IV.4). No interaction between storage time and packaging condition was observed. DI rapidly increased from day 1 to day 6 on cherry tomatoes stored without a sachet, being such increment less pronounced in samples including sachets (Figure IV.4A). The SK sachet was effective to control grey mould during the first 21 days of storage. The effect of 0.04T, 0.09T and 0.19T sachets was similar to that of the SK sachet, showing a global mean DI decrease of approximately 36 % compared with tomatoes without sachet treatment. Nevertheless, the mean DI on tomatoes stored with a 0.38T sachet was 14 % higher compared with the SK sachet. Taking into account that EOs may affect plant cells and exhibit a dose-dependent phytotoxic activity (López-Reyes et al., 2013), that sachet with the highest thymol dose may have led to a higher leakage of intracellular compounds favouring a higher microbial growth.

On the other hand, the combination of the SK and T agents resulted in a higher incidence and severity of decay compared with the respective individual effects (Figure IV.4B). In this sense, the SK+0.38T sachet led to the highest mean DI (as previously observed in 0.38T samples) followed by SK+0.09T, SK+0.19T and finally SK+0.04T. Nevertheless, contrary to that observed *in vitro*, the DI of samples including ET-carrying sachets (Figure IV.4C) was lower compared with those exposed to T (Figure IV.4B), without differences among ET doses. These results suggest that the increased tomato susceptibility to grey mould was due to a plant cell sensitivity resulting from the interaction of the SK and T agents with the food matrix, which could be overcome when thymol was encapsulated (Campolo et al.,

2020). In accordance, it was suggested that thymol may trigger a mild stress-like signal on the tomato to build an induced resistance system (Mirdehghan & Valero, 2017).

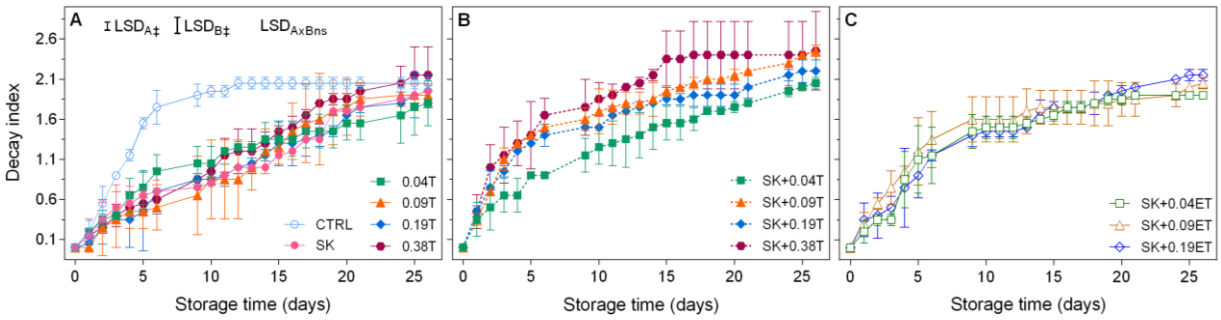

Figure IV.4. Incidence and severity on cherry tomatoes artificially infected with *Botrytis cinerea* conidia and stored at 11 °C up to 26 days in the absence of a treatment sachet (CTRL), under $KMnO_4$-loaded sepiolite (SK) and different doses of thymol (B); under SK+T ($KMnO_4$-loaded sepiolite and thymol; B); and under SK+ET ($KMnO_4$-loaded sepiolite and encapsulated thymol; C) sachets (mean (n=3)±standard deviation). The uppercase letters (subscripts) A and B denote the packaging system and incubation time factors, respectively. ns and ‡ significance for $P \leq$ not significant and 0.001, respectively. LSD: Least significant difference (source: Own elaboration).

On the other hand, some signalling pathways of plant-induced defence are C_2H_4-dependent, particularly those involved in defence against necrotrophic pathogens such as *B. cinerea* (AbuQamar et al., 2017). Thus, when C_2H_4 was also removed from the packing atmosphere, plant defence mechanisms could be limited, giving the fungus the chance to infect and reproduce.

IV.3.3 Effect of active sachets on tomato fruit quality during postharvest storage

IV.3.3.1 Weight loss

Weight loss was significant both after cold storage (11 °C) and commercialization periods (+3 days at 22 °C), being the loss increments dependent on the packaging technology used. Moreover, a significant interaction was observed between the packaging conditions and storage time. Weight loss was very low (<1 %) after 28 days at 11 ºC (data not shown), as it is generally expected in horticultural products stored under high RH, which in our case was reached due to packaging. Similarly, weight losses below 0.7 % were observed in cherry tomatoes under flow-packaging after 28 days at 8 ºC (Buendía−Moreno, Ros−Chumillas, et al., 2019). In contrast, weight losses higher than 10 % were reported in unpackaged cherry tomatoes after 25 days at 5 °C (Fagundes et al., 2015). Furthermore, Guillén et al. (2006) also found weight losses of 8–12 % in unpackaged cherry tomatoes after 28 days at 10 °C.

After 28 days at 11 ºC + 3 days at 22 °C, weight loss of CTRL samples increased to 1.1 % while it was highly reduced when sachets were used (< 0.4 %), without differences among them (Figure IV.5). These results agree with reports for apricot, where it was observed that C_2H_4 scavengers reduced fruit weight loss both in MAP at 2 °C and under air conditions at 15 °C (Álvarez-Hernández et al., 2020). Such weight retention was attributed to a probably reduced cell wall detriment, resulting from the C_2H_4 removal.

IV.3.3.2 Fruit firmness

Tomato firmness decreased throughout the assayed storage periods (Table IV.2). Particularly, firmness decreased by 1.6-4, 3-5, 4-6 and 5-7 N after 7, 13, 21 and 28 days at 11 °C, respectively, in a packaging condition-dependent manner. After complementary 3 days at 22 °C, firmness was slightly decreased (< 2 N) without differences among treatments.

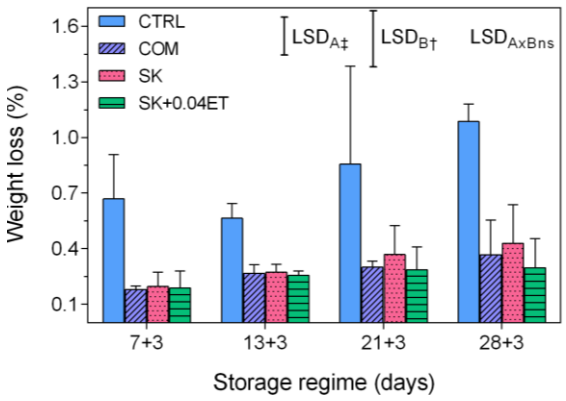

Figure IV.5. Weight loss of cherry tomato fruit during storage at 11 °C for 7, 13, 21 and 28 days plus 3 days at 22 °C under different packaging systems (mean (n=3)±standard deviation). The uppercase letters (subscripts) A and B denote the packaging system and storage time factors, respectively. ns, † and ‡ significance for *P* ≤ not significant, 0.01, and 0.001, respectively. LSD: Least significant difference (source: Own elaboration).

Some EOs have shown, among other properties, an inhibitory effect of cell wall-degrading enzymatic activity allowing firmness preservation during storage of different horticultural products (Serrano et al., 2005). Nevertheless, EOs and their components may also have cytotoxic activity and adverse sensory effects in foods. Thymol/eugenol and thyme essential oil treatments enhanced odour, browning, and tissue softening in fresh-cut lettuce (Viacava et al., 2018; Yuan et al., 2019). Furthermore, the shellac-coating ability to maintain grapefruit firmness was reduced when thymol was added (Yan et al., 2020). To alleviate such negative impacts, lower concentrations of thyme essential oil were used, as well as a microencapsulation technique (Bagamboula et al., 2004; Viacava et al., 2018). Thus, the pronounced firmness loss observed in the SK+0.04ET-treated cherry tomatoes at the

beginning of storage is probably due to a toxicity effect resulting from an uncontrolled thymol vapour release (as reviewed by Otoni et al. (2016)).

IV.3.3.3 Colour

As shown in Table IV.3, the colour index values of tomato increased throughout cold storage (an average of 0.6 and 22.3 CI and COL units, respectively) and commercialization periods (approximately 0.7 and 23.0 CI and COL units, respectively). The packaging condition influenced the CI and COL changes throughout the two storage regimes studied, especially at 11 °C ($P \leq 0.001$). No high colour differences were observed on day 28, and its complimentary commercialization period, among the different assayed packaging conditions. Such colour changes of tomato are explained due to the increment of carotenoids contents like lycopene (responsible for tomato red colour), β−carotene (orange colour) and ζ−carotene (pale−yellow colour) during ripening, and to a subsequent decrease toward senescence (Fraser et al., 1994; López & Gómez, 2004).

The tomato colour is the main purchase−decision factor as stated by 80 % of the consumers from a consumer study on tomato preferences (Serrano-Megias & López-Nicolás, 2006). Nevertheless, the correlation of CIELAB colour components (*L*, a** and *b**) with sensory colour data is better conducted using a unique colour index that must be carefully selected for each specific horticultural product (Pathare et al., 2013). Thus, the CI parameter was hereby selected to analyse the tomato ripeness as previously recommended (López & Gómez, 2004).

The CI increased during cold storage as the tomatoes ripened. Overall, the sachets containing only an C_2H_4 scavenger did not show any colour alteration during storage. Meanwhile, during the first 21 days of storage at 11 °C, tomatoes packed with a SK+0.04ET sachet showed higher CI values than CTRL samples. These results agree with reports for lettuce, where thymol-based treatments led to colour-darkening associated with the cytotoxic activity (Bagamboula et al., 2004; Yuan et al., 2019). Mirdehghan & Valero, (2017) stated that EOs components such as thymol and eugenol may increase bioactive compounds in tomato fruit, including lycopene and phenolics. The latter authors related such behaviour to the fact that thymol acts as a signalling compound to induce a plant-induced resistance, as described in section 3.2.2.

Results suggested that C_2H_4 scavenging would not compromise the colour quality of tomato during the studied storage periods. But if in addition to the C_2H_4 removal, thymol is released, then the antioxidant defence system may be enhanced causing colour changes.

Table IV.2. Fruit firmness, total soluble solids content, titratable acidity and pH of cherry tomato fruit during storage at 11 °C up to 28 days and holding at 22 °C for 3 days under different packaging systems (see Table IV.1) (mean (n=3)±standard deviation) (source: Own elaboration).

Storage time (days)	**Packaging system**	**Firmness (N)**		**SSC (%)**		**TA (g L^{-1})**		**pH**	
		19.2 ± 0.9		6.6 ± 0.2		6.6 ± 0.2		3.9 ± 0.1	
		At 11 °C	+3 days at 22 °C	At 11 °C	+3 days at 22 °C	At 11 °C	+3 days at 22 °C	At 11 °C	+3 days at 22 °C
7	CTRL	17.2 ± 0.4	14.6 ± 0.3	6.4 ± 0.2	6.5 ± 0.2	6.5 ± 0.8	4.6 ± 0.3	4.0 ± 0.1	4.1 ± 0.0
	COM	17.6 ± 0.7	14.3 ± 0.6	6.3 ± 0.2	6.2 ± 0.4	6.4 ± 0.7	4.0 ± 0.4	4.0 ± 0.0	4.1 ± 0.1
	SK	16.2 ± 1.0	14.1 ± 1.1	5.9 ± 0.4	6.3 ± 0.6	6.0 ± 0.3	4.8 ± 0.9	4.0 ± 0.1	4.1 ± 0.0
	SK+0.04ET	15.0 ± 0.9	12.7 ± 0.1	6.4 ± 0.1	6.2 ± 0.5	7.9 ± 0.7	3.7 ± 0.7	4.0 ± 0.1	4.1 ± 0.1
13	CTRL	15.8 ± 0.7	13.5 ± 0.9	6.2 ± 0.0	6.4 ± 0.1	5.5 ± 0.6	5.2 ± 0.0	4.0 ± 0.1	4.1 ± 0.1
	COM	15.8 ± 1.1	13.4 ± 1.0	5.9 ± 0.5	6.1 ± 0.3	5.7 ± 0.5	4.8 ± 0.7	4.0 ± 0.1	4.2 ± 0.0
	SK	15.2 ± 1.0	15.1 ± 0.3	6.1 ± 0.3	6.5 ± 0.4	5.6 ± 0.9	6.2 ± 0.4	3.9 ± 0.1	4.1 ± 0.1
	SK+0.04ET	13.8 ± 0.8	12.8 ± 0.3	5.9 ± 0.2	6.3 ± 0.2	5.7 ± 0.4	8.1 ± 0.6	4.0 ± 0.1	4.1 ± 0.1
21	CTRL	14.0 ± 0.9	13.3 ± 0.0	6.4 ± 0.0	6.4 ± 0.3	6.4 ± 0.2	6.5 ± 0.6	4.1 ± 0.0	4.2 ± 0.1
	COM	14.7 ± 0.2	12.5 ± 0.6	6.3 ± 0.1	5.8 ± 0.6	6.2 ± 0.2	3.9 ± 0.4	4.1 ± 0.1	4.2 ± 0.1
	SK	14.8 ± 0.8	12.9 ± 0.6	6.3 ± 0.1	6.5 ± 0.2	6.0 ± 0.5	4.9 ± 0.9	4.2 ± 0.1	4.2 ± 0.0
	SK+0.04ET	13.3 ± 0.4	12.9 ± 0.2	6.4 ± 0.7	6.1 ± 0.5	6.1 ± 0.6	5.3 ± 0.7	4.1 ± 0.1	4.2 ± 0.1

Table IV.2. Continued.

Storage time (days)	Packaging system	Firmness (N)		SSC (%)		TA (g L^{-1})		pH	
28	CTRL	12.4 ± 0.6	13.6 ± 0.4	6.4 ± 0.0	5.7 ± 0.2	5.3 ± 0.2	5.0 ± 0.6	4.2 ± 0.1	4.3 ± 0.1
	COM	14.4 ± 0.7	16.4 ± 0.8	6.1 ± 0.4	6.1 ± 0.3	5.3 ± 0.4	5.2 ± 0.7	4.2 ± 0.0	4.2 ± 0.1
	SK	13.5 ± 0.9	12.0 ± 0.3	5.9 ± 0.5	5.9 ± 0.3	5.3 ± 0.6	5.5 ± 0.6	4.2 ± 0.0	4.2 ± 0.1
	SK+0.04ET	12.6 ± 0.6	17.0 ± 0.7	6.7 ± 0.6	6.1 ± 0.5	4.4 ± 0.4	5.2 ± 0.7	4.2 ± 0.0	4.3 ± 0.1
Packaging system (A)		(1.0)‡	ns	ns	ns	ns	(0.7)‡	ns	ns
Storage time (B)		(1.2)‡	(1.0)‡	(0.3)†	(0.4)†	(0.7)‡	(0.8)‡	(0.1)‡	(0.1)‡
A×B		ns	(2.0)‡	ns	ns	(1.1)†	(1.6)‡	ns	ns

SSC: Total soluble solids content; TA: Titratable acidity.
Values within parentheses represent the least significant difference. ns, †, ‡ significance for $P \leq$ not significant, 0.05, 0.01, and 0.001, respectively.

Table IV.3. Skin colour values of cherry tomato fruit during storage at 11 °C up to 28 days and after 3 additional days at 22 °C under different packaging systems (see Table IV.1) (mean (n=3)±standard deviation) (source: Own elaboration).

Storage Time (days)	Packaging system	CI (*a*/b**)		COL ((2,000×*a**)(*L**×*C**))	
		0.3 ± 0.0		12.2 ± 1.6	
		At 11 °C	+3 days at 22 °C	At 11 °C	+3 days at 22 °C
7	CTRL	0.5 ± 0.0	0.7 ± 0.0	20.7 ± 1.7	29.0 ± 1.4
	COM	0.5 ± 0.0	0.7 ± 0.0	23.1 ± 1.3	28.5 ± 0.9
	SK	0.5 ± 0.0	0.7 ± 0.1	20.3 ± 1.4	29.3 ± 2.3
	SK+0.04ET	0.6 ± 0.0	0.8 ± 0.1	25.1 ± 1.1	31.7 ± 1.8
13	CTRL	0.6 ± 0.1	0.8 ± 0.0	25.6 ± 1.6	30.6 ± 1.4
	COM	0.7 ± 0.0	0.8 ± 0.0	27.1 ± 1.4	31.2 ± 0.9
	SK	0.7 ± 0.1	0.8 ± 0.0	27.0 ± 2.9	30.6 ± 0.6
	SK+0.04ET	0.8 ± 0.0	0.9 ± 0.0	30.5 ± 0.6	33.7 ± 0.4
21	CTRL	0.8 ± 0.0	1.0 ± 0.0	31.3 ± 0.6	35.1 ± 0.4
	COM	0.8 ± 0.0	0.9 ± 0.0	31.1 ± 0.8	34.5 ± 0.6
	SK	0.8 ± 0.0	0.9 ± 0.1	31.0 ± 0.2	33.8 ± 2.3
	SK+0.04ET	0.9 ± 0.0	0.9 ± 0.1	32.9 ± 0.5	34.0 ± 1.4
28	CTRL	0.9 ± 0.0	1.0 ± 0.0	34.5 ± 0.8	35.2 ± 0.0
	COM	0.9 ± 0.0	1.0 ± 0.0	33.3 ± 0.7	35.4 ± 0.0
	SK	0.9 ± 0.0	0.9 ± 0.0	33.8 ± 0.4	34.9 ± 0.0
	SK+0.04ET	0.9 ± 0.0	1.0 ± 0.0	34.8 ± 0.4	35.6 ± 0.0
Packaging condition (A)		(0.0)‡	(0.0)*	(1.7)‡	(1.0)*
Storage time (B)		(0.1)‡	(0.1)‡	(1.9)‡	(1.9)‡
A×B		(0.1)†	ns	(2.2)*	ns

CI; Colour index; COL: Tomato colour index.
Values within parentheses represent the least significant difference. ns, *, †, ‡ significance for $P \leq$ not significant, 0.05, 0.01, and 0.001, respectively.

IV.3.3.4 Soluble solids concentration, titratable acidity and pH

Initial mean SSC, TA and pH levels of 6.6 %, 6.6 g L^{-1} and 3.9, respectively, were registered (Table IV.2). SSC of our samples was in the range (4-8 %) of previous reports about different tomato varieties including cherry tomato (Buendía−Moreno, Soto−Jover, et al., 2019), where preharvest factors (variety, climate, irrigation conditions, soil conditions, etc.) shown a high influence in the sugar content of horticultural products (Antolinos et al., 2020; Bertin & Génard, 2018). In general, sugars of plant products are consumed as an energy source during postharvest life because of product respiration (Kader, 2002). Accordingly, a slight SSC decrease (0.3-0.7 %; $P \leq 0.01$) was hereby observed at day 7, being such reductions lower than < 0.4 % after the remaining cold storage period, and their respective commercialization periods. Similar to our results, no high SSC changes (< 0.3 %) were observed in different tomato varieties, including cherry tomato, during cold storage, and even after commercialization periods at 22 ºC (Buendía−Moreno et al., 2020; García-García et al., 2013; Guillén et al., 2006). In that sense, the packaging of tomatoes is crucial to reduce sugar loss during storage since the respiration of samples may be decreased.

Tomato overall quality is mainly influenced by TA (88 %) while SSC also determines tomato overall quality (60 %) and sweetness (76 %) (Stevens et al., 1979). TA of samples with treatment sachets was not affected during storage at 11 ºC (Table IV.2). Nevertheless, TA decreases of 2-4 g L^{-1} were observed after 3 days at 22 ºC in tomatoes previously kept at 11 °C for 7 days, regardless of the packaging treatments. After complimentary periods, TA slight increments were observed in tomatoes exposed to an SK and SK+0.04ET sachet (0.6 and 2.4 units, respectively) for 13 days at 11 °C, as compared with CTRL and COM samples. At the end of the cold storage period, TA decreased of all the samples decreased by 1-2 g L^{-1}, without changes after commercialization periods.

The organic acid reduction during postharvest life is related to their use as respiration substrates during product ripening as occurred for sugars (Kader & Ben-Yehoshua, 2000; Ortiz et al., 2013). Hence, organic acids of cherry tomato (mainly citric and malic acids) were reduced by 40-60 % after 25 days at 5 °C (Fagundes et al., 2015). On the other hand, because the SSC was relatively stable throughout the two storage regimes studied, the TA increments observed for tomatoes subjected to an SK-including treatment during 13 days at 11 °C + 3 days at 22 °C could be associated with the high C_2H_4 oxidation power of SK (Álvarez-Hernández et al., 2020). In this sense, the C_2H_4 oxidation by $KMnO_4$ gives rise to CO_2 generation, which is involved in the malic formation (Murata & Minamide, 1970). Thus, it can be deduced that the greater the C_2H_4 oxidation, the greater the CO_2 generation; and the higher the CO_2 concentration, the higher organic acidity. Correspondingly to TA, pH of

samples slightly increased approximately 0.3 units after 28 days at 11 °C. As similarly observed for SSC, packaging treatment and packaging treatment×storage time were not significant for pH values (Table IV.2).

Overall, these results suggest that the use of treatment sachets did not considerably compromise tomato physicochemical quality, which was well preserved during the shelf-life periods assayed.

IV.3.3.5 Sensory evaluation

The sensory quality of tomatoes was highly maintained throughout 28 days at 11 ºC + 3 days at 22 ºC despite the packaging condition used, reporting overall quality scores ranging from 4 to 4.5 (Figure IV.6). Flavour (Pearson correlation: 0.697) and hardness (0.398) have a key role in the sensory acceptability of tomatoes (Serrano-Megias & López-Nicolás, 2006). In that sense, the highest differences among treatments were found for the fruit flavour property being the SK-treated tomatoes scored with the highest flavour score (4.5) after 28 days at 11 ºC, although the remaining samples were still highly scored with values of 3.5-4.

Attending to mouthfeel texture, all the assayed sachets led to similar scores of 4.2, while the CTRL fruit was scored with 3.7 after 28 days at 11 ºC. Similarly, no high differences in mouthfeel texture were perceived among the different tomato samples fruit after 28 days at 11 ºC + 3 days at 22 ºC. Visual appearance scores of all the samples were very similar (close to 5) after 28 days at 11 ºC, and + 3 days at 22 ºC, which agree with colour data (Table IV.3). Shrivelling was practically unnoticed in all the fruit samples, after both cold storage and commercialization periods (Figure IV.6), which is in agreement with weight losses (Figure IV.5).

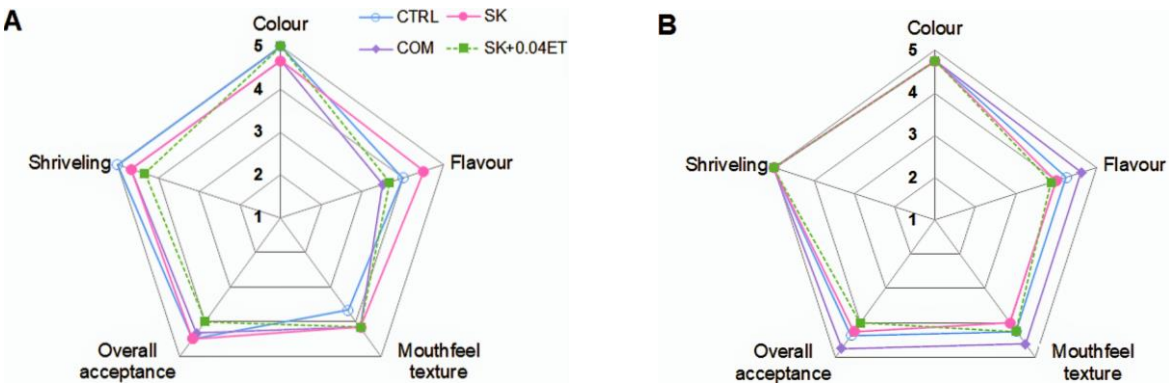

Figure IV.6. Sensory quality of cherry tomatoes stored during storage at 11 ºC for 28 days (A) and holding at 22 °C for 3 days (B) under different packaging systems (see Table IV.1) (mean (n=3)) (source: Own elaboration).

Interestingly, the measured higher weigh losses of CTRL samples, compared with fruit exposed to a sachet (≈ 1%) for 28 days at 11 ºC + 3 days at 22 ºC (Figure IV.6), was still very low to be perceived by panellists according to shrivelling scores. Overall, tomatoes maintained a good sensory quality for at least 28 days at 11 ºC, and after its respective commercialization period of 3 days at 22 ºC, regardless of the sachet-based packaging technology used.

As mentioned above, EOs may damage plant cells of horticultural products (López-Reyes et al., 2013), reducing the product quality and consequently affecting consumer acceptance. Nevertheless, despite the adverse effect of thymol elucidated through tomato fruit firmness and colour measurements, sensory records (which are in accordance with weight loss and physicochemical quality data) indicate that the use of thymol-including sachets would not compromise the consumer's acceptance.

IV.3.3.6 Mathematical modelling of quality degradation processes

Since fruit weight, firmness, pH, TA, CI and COL features of cherry tomatoes stored at 11 °C showed significant changes over time ($P \leq 0.001$), they were used to assess the ability of the zero- and first-order kinetic and Weibull models to describe the quality degradation of cherry tomato fruit. In general, the zero-order kinetic and Weibull models were the best to fit quality changes in tomato (Table IV.4). The zero-order kinetic fit converged all the experimental data, being the best suited for describing the kinetics of the tomato colour-related features. Meanwhile, the Weibull model was best to fit the firmness data of all the tomato samples, as well as the TA kinetics of the SK-treated fruit sample.

Regarding the weight losses, both models were suitable for fitting data of fruit exposed to SK and SK+0.04ET sachets, with high adj. R^2 (≥ 0.990) and low RMSE values (≤ 0.003). These results imply that the rate of such features increased or decreased as a function of time, showing a variation among the assayed packaging conditions. The parameter estimates derived for the quality attributes, along with the corresponding 95 % confidence levels, are presented in Table IV.5. The remaining data did not show particular changes that could be described by the evaluated models ($R^2 < 0.800$). Particularly, the firmness and CI of tomatoes could be modelled, regardless of the packaging condition used.

Among the samples, CTRL fruit data showed the narrowest confidence intervals, being the most auspicious to estimate firmness and colour changes. On the contrary, the confidence bands of the SK+0.04ET-treated fruit for the CI attribute became too wider at the end of the fitted curve (data not shown), supplying a less precise estimate.

Table IV.4. Goodness-of-fit of zero and first kinetics and Weibull models for time-dependent quality attribute data of cherry tomatoes under different packaging systems (see Table IV.1) up to 28 days at 11 °C (source: Own elaboration).

Quality attribute (unit)	Packaging system	Model	Adj. R^2	SSE	RMSE
Weight (g)	SK	Zero-order kinetic	0.992	0.000	0.003
		Weibull	0.994	0.000	0.002
	SK+0.04ET	Zero-order kinetic	0.990	0.000	0.001
		Weibull	0.993	0.000	0.001
Firmness (N)	CTRL	Zero-order kinetic	0.997	0.116	0.197
		Weibull	0.998	0.047	0.153
	COM	Zero-order kinetic	0.923	2.152	0.847
		Weibull	0.946	1.015	0.713
	SK	Zero-order kinetic	0.859	2.362	0.887
		Weibull	0.966	0.374	0.432
	SK+0.04ET	Weibull	0.992	0.167	0.289
TA (g citric acid L^{-1})	SK	Weibull	0.815	0.626	0.560
CI	CTRL	Zero-order kinetic	0.977	5.392	1.341
		First-order kinetic	0.889	25.543	2.918
	COM	Zero-order kinetic	0.930	14.094	2.167
		First-order kinetic	0.855	29.202	3.120
	SK	Zero-order kinetic	0.950	14.740	2.217
		First-order kinetic	0.850	44.541	3.853
	SK+0.04ET	Zero-order kinetic	0.820	56.975	4.358
COL	CTRL	Zero-order kinetic	0.949	7.577	1.589
	COM	Zero-order kinetic	0.874	16.838	2.369
	SK	Zero-order kinetic	0.863	26.028	2.946

TA: Titratable acidity; CI: Colour index; COL: Tomato colour index; Adj. R^2: Adjusted coefficient of determination; SSE: sum of squared errors; RMSE: the root mean squared error.

In agreement with the small fitting errors observed (Table IV.1), the tight weight confidence intervals of fruit exposed to SK and SK+0.004ET sachets, as well as the narrow firmness intervals of all the samples validate the Weibull modelling estimation accuracy (Table IV.5).

Finally, to determine the precision of the Weibull model to predict firmness values, the prediction intervals were obtained. The 95 % prediction bands plot suggested that the modelling equations were sufficiently accurate in predicting the firmness behaviour of the tomato under different packaging conditions, at any time during storage at 11 °C (Figure IV.7). Nevertheless, it should be noted that whereas the prediction bands for the CTRL samples were close to the experimental values indicating a good precision of the model's predictions, the rest of the samples did not have such accuracy—especially in the case of the COM-treated fruit.

The zero and first-order kinetics are conventionally used to describe food degradation reactions. However, in agreement with Amodio et al. (2013), the Weibull model also showed an ability to characterise quality changes of cherry tomatoes, with even higher accuracy than the zero and first-order models. Particularly, the Weibull model fitted well firmness changes of tomatoes packed under different conditions, which is of interest as these changes have a direct impact on the acceptability of such product (Buendía−Moreno et al., 2020). According to this model, the firmness loss rate of the CTRL sample (0.016 $days^{-1}$) decreased when an active sachet was used, with a mean degradation rate of 0.003, 0.004 and 0.009 $days^{-1}$ for tomatoes exposed to SK+0.04ET, SK and COM treatments, respectively. This means that the sachets were able to delay the firmness loss rate in cherry tomatoes, particularly the SK+0.04ET and SK ones.

Table IV.5. Model parameter estimates for quality attribute changes in cherry tomatoes stored at 11 °C under different packaging conditions (see Table IV.1) (source: Own elaboration).

Quality attribute (unit)	Packaging system	Model	Parameters	Estimates	SEE	95 % confidence level
Weight (g)	SK	Zero-order kinetic	C_0	190.88	0.05	190.73 – 191.03
			k	0.06	0.00	0.05 – 0.07
		Weibull	C_0	190.92	0.05	190.69 – 191.15
			α	5293.77	2467.31	-5322.22 – 15909.77
			β	0.89	0.08	0.55 – 1.24
	SK+0.04ET	Zero-order kinetic	C_0	184.15	0.03	184.04 – 184.25
			k	0.04	0.00	0.03 – 0.04
		Weibull	C_0	184.18	0.04	184.02 – 184.33
			α	9639.76	5533.99	-14171.08 – 33450.60
			β	0.88	0.09	0.50 – 1.26
Firmness (N)	CTRL	Weibull	C_0	19.12	0.14	18.53 – 19.72
			α	64.34	2.41	53.98 – 74.70
			β	1.03	0.05	0.83 – 1.22
	COM	Weibull	C_0	19.31	0.66	16.48 – 22.14
			α	116.15	49.50	-96.85 – 329.15

Table IV.5. Continued.

Quality attribute (unit)	Packaging system	Model	Parameters	Estimates	SEE	95 % confidence level
			β	0.77	0.23	-0.20 – 1.75
	SK	Weibull	C_0	19.16	0.40	17.42 – 20.89
			α	235.39	136.56	-352.17 – 822.96
			β	0.52	0.13	-0.03 – 1.07
	SK+0.04ET	Weibull	C_0	19.17	0.27	18.01 – 20.33
			α	325.94	125.30	-213.16 – 865.05
			β	0.36	0.05	0.14 – 0.58
TA (g citric acid L^{-1})	SK	Weibull	C_0	6.56	0.11	6.10 – 7.02
			α	1533.43	5297.09	-21258.11 – 24324.98
			β	0.44	0.33	-0.99 – 1.88
CI	CTRL	Zero-order kinetic	C_0	0.29	0.04	0.17 – 0.41
			k	-0.02	0.00	-0.03 – -0.02
	COM	Zero-order kinetic	C_0	0.33	0.06	0.14 – 0.52
			k	-0.02	0.00	-0.03 – -0.01
	SK	Zero-order kinetic	C_0	0.32	0.06	0.14 – 0.50
			k	-0.02	0.00	-0.03 – -0.01

Table IV.5. Continued.

Quality attribute (unit)	Packaging system	Model	Parameters	Estimates	SEE	95 % confidence level
	SK+0.04ET	Zero-order kinetic	C_0	0.44	0.11	0.10 – 0.77
			k	-0.02	0.00	-0.03 – -0.01
COL	CTRL	Zero-order kinetic	C_0	14.66	1.87	8.72 – 20.61
			k	-0.75	0.09	-1.03 – -0.48
	COM	Zero-order kinetic	C_0	16.83	2.51	8.86 – 24.80
			k	-0.63	0.12	-1.00 – -0.25
	SK	Zero-order kinetic	C_0	17.48	2.69	8..92 – 26.04
			k	-0.63	0.12	-1.02 – -0.24

SEE: Standard error of the estimate; CI: Colour index *a*/b**; COL: Tomato colour index; C_0: Initial quality of the cherry tomato; k: Rate constant or quality degradation coefficient; α: Scale factor (in days); β: shape factor (dimensionless).

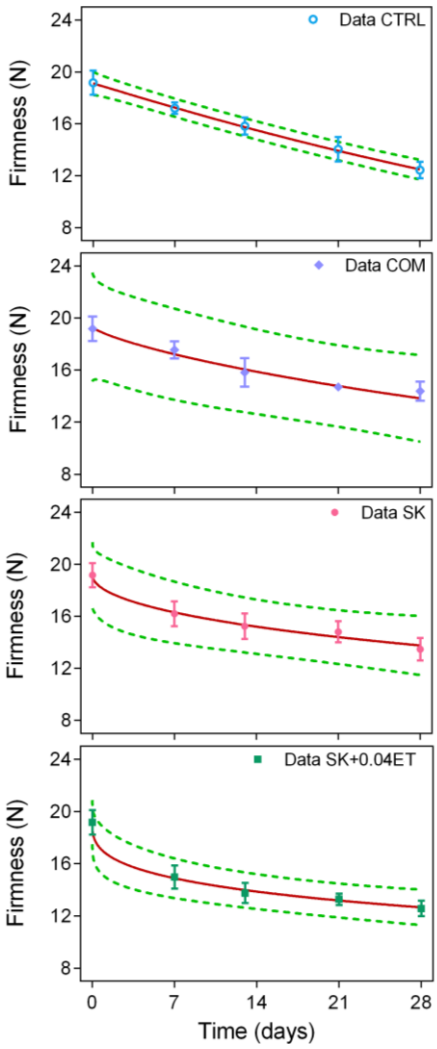

Figure IV.7. Fitting of experimental firmness data (mean (n=3)±standard deviation) using the Weibull model for cherry tomato fruit stored at 11 °C under different packaging conditions (see Table IV.1). Solid red lines show the fitted curves, while the broken green lines delimit 95 % prediction intervals (source: Own elaboration).

IV.4 Conclusions of this chapter

From *in vitro* assays, sachets carrying thymol (from 0.04 to 0.38 g) were effective in inhibiting *B. cinerea* development, but thymol encapsulation limited such antifungal activity. Meanwhile, C_2H_4 scavenging did not show any significant effect against such pathogen. In contrast, whereas both thymol release- and C_2H_4 removal-based techniques indistinctly restrained the *B. cinerea* infection on fresh cherry tomatoes, the combination of such techniques resulted in an increased tomato susceptibly. This effect could be lessened by encapsulating thymol. Lower thymol concentrations than those used here are encouraged to be assayed since even 0.04-g thymol+C_2H_4 scavenger revealed enhanced fruit softening and colour changes —although they were so slight as to be perceived by the sensory panel.

Our results showed that C_2H_4 scavenging technologies may provide an efficient alternative to improve food safety for fresh cherry tomato fruit, without compromising its quality attributes. Furthermore, our findings highlight the importance of removing C_2H_4 from the atmosphere surrounding horticultural products since C_2H_4-scavenging sachets were effective in controlling grey mould and slowing down fruit weight loss during postharvest storage. Particularly, the developed C_2H_4 scavenger —consisting of a $KMnO_4$-loaded SP— stood out for its ability to preserve a good flavour consumer's perception even after 28 days at 11 ºC + 3 days at 22 °C.

During postharvest storage, no alteration was detected in the sensory properties of tomato fruit when it was exposed to an C_2H_4 scavenger or a 0.04-g thymol+ C_2H_4 scavenger system. The kinetics of changes in quality attributes of cherry tomatoes during cold storage followed Weibull and zero-order models. Then, the here prepared C_2H_4 scavenger-carrying sachets have potential to be used as antifungal active-packaging technology to preserve the quality of fresh produce. Further work is needed to elucidate the thymol phytotoxicity mechanisms and the metabolic processes triggered when EOs and C_2H_4 scavenging tools are used in parallel.

GENERAL CONCLUSIONS

GENERAL CONCLUSIONS

In this PhD Thesis, we provide two alternative C_2H_4 scavengers consisting of a $KMnO_4$-impregnated acidified porous mineral, either SP or MMT. These materials showed the ability to preserve fruit freshness for longer and potentially, reduce food loss and waste. In accordance, the resulting materials suggest a high cost-effectiveness ratio and convenience, which makes them promising to be applied in commercial scavenging systems. This kind of postharvest tools has special importance when it comes to exporting C_2H_4 sensitive fresh or minimally processed produce, or when it is required to store it for lengthy periods —as when it comes to seasonal fruit.

The $KMnO_4$-based C_2H_4 scavenging systems have been shown as a good option for packaging fresh horticultural commodities. The here assayed C_2H_4 scavengers revealed a temperature-dependent activity, being the highest activity observed near the C_2H_4 critical temperature (9.9 °C). Therefore, the here developed tools can be used during cold chain management.

By supporting $KMnO_4$ onto acid-treated MMT and SP, approximately 10.2 and 9.8 L kg^{-1} C_2H_4 removal can be achieved at 22 °C, respectively. In this kind of systems, the $KMnO_4$ is the C_2H_4 oxidizing agent, while the porous support promotes the C_2H_4 scavenging activity. We observed that the C_2H_4 scavenger preparation conditions greatly influenced the physical features of the final tools. Hydrochloric acid at a concentration lower than 1 M was effective to improve the surface properties of such clays and, in particular, increasing the contact area.

Both $KMnO_4$-loaded MMT and SP carried in Tyvek® sachets were able to reduce in-package C_2H_4 concentrations and maintain postharvest quality and safety of packaged fruit. Besides, the here developed C_2H_4 scavengers provided a more favourable in–package gaseous composition than the commercial one used — which comprises zeolite as $KMnO_4$ support.

The two loaded clays proved to be effective in both MAP and conventional air packaging, at temperatures as low as 2 °C or as high as 22 °C. Specifically, the $KMnO_4$-loaded MMT was able to delay the fungal decay incidence on fresh blueberry fruit under MAP storage at 2 ºC and then, to increase the shelf-life of such fruit. Meanwhile, the $KMnO_4$-loaded SP was useful to slow down the quality loss in apricot fruit during storage in MAP at 2ºC and under air conditions at 15 ºC.

On the other hand, the $KMnO_4$-loaded SP did not show any effect against *B. cinerea* under *in vitro* conditions. On the contrary, when a pathogenicity test was performed, the $KMnO_4$-loaded SP was found to control the grey mould disease on fresh cherry tomatoes. Nevertheless, the combination of such C_2H_4 removal tool with a thymol release technique led to an increased tomato susceptibly to *B. cinerea*. When the $KMnO_4$-loaded SP effect was assayed on cherry tomato fruit, the grey mould was controlled, the fruit weight loss was slowed down and the good flavour consumer's perception was preserved during storage at 11 °C and after 3 days at 22 °C.

None of the here prepared C_2H_4 scavengers had detrimental effects on the food quality of blueberry, apricot or tomato *cherry*. Then, the prepared C_2H_4 scavengers have the potential to be used as antifungal active-packaging technology. Nevertheless, combining C_2H_4 scavenging systems with thymol release systems is not recommended since it seems to weaken the plant defence system. Further research and innovation are needed to optimize the C_2H_4 scavenger preparation methods, as well as to enhance product application efficiency. Besides, it is encouraged to study the fruit metabolic response to the C_2H_4 removal along with the thymol release.

SCIENTIFIC PUBLICATIONS DERIVED FROM THIS PhD THESIS

DERIVED SCIENTIFIC PUBLICATIONS FROM THIS PhD THESIS

The following publications included in JCR-SCI Journals have directly derived from the research activities performed in this PhD Thesis:

- Álvarez–Hernández, M.H., Artés–Hernández, F., Ávalos–Belmontes, F., Castillo–Campohermoso, M.A., Contreras–Esquivel, J.C., Ventura–Sobrevilla, J.M., Martínez–Hernández, G.B. 2018. Current scenario of adsorbent materials used in ethylene scavenging systems to extend fruit and vegetable postharvest life. Food and Bioprocess Technology, 11, 511–525. https://doi.org/10.1007/s11947-018-2076-7

- Álvarez-Hernández, M.H., Martínez-Hernández, G.B., Avalos-Belmontes, F., Rodríguez-Hernández, A.M., Castillo-Campohermoso, M.A., Artés-Hernández, F. 2019. An Innovative ethylene scrubber made of potassium permanganate loaded on a protonated montmorillonite: A case study on blueberries. Food and Bioprocess Technology, 12, 524–538. https://doi.org/10.1007/s11947-018-2224-0

- Martínez-Hernández, G.B., Álvarez-Hernández, M.H., Artés-Hernández, F. 2019. Browning control using cyclodextrins in high pressure–treated apple juice. Food and Bioprocess Technology, 12, 694–703. https://doi.org/10.1007/s11947-019-2242-6

- Álvarez-Hernández, M.H., Martínez-Hernández, G.B., Avalos-Belmontes, F., Castillo-Campohermoso, M.A., Contreras-Esquivel, J.C., Artés-Hernández, F. 2019. Potassium permanganate-based ethylene scavengers for fresh horticultural produce as an active packaging. Food Engineering Reviews 11, 159–183. https://doi.org/10.1007/s12393-019-09193-0

- Álvarez-Hernández, M.H., Martínez-Hernández, G.B., Avalos-Belmontes, F., Miranda-Molina, F.D., Artés-Hernández, F. 2020. Postharvest quality retention of apricots by using a novel sepiolite–loaded potassium permanganate ethylene scavenger. Postharvest Biology and Technology, 160, 111061. https://doi.org/10.1016/j.postharvbio.2019.111061

The following research works have been published in Scientific meetings:

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- Álvarez-Hernández, M.H., Martínez-Hernández, G.B., Avalos-Belmontes, F., Artés-Hernández, F. 2019. Effects of an innovative potassium permanganate-based ethylene scavenger during blueberry storage. In F. Artés-Hernández, J.A. Fernández-Hernández, J.E. Cos, J.J. Alarcón, M. Egea-Cortines, E. Aguayo (Eds.). Proceedings of the 7th Workshop on Agri-Food Research for young researchers. CRAI Biblioteca, Universidad Politécnica de Cartagena, Cartagena, Murcia, Spain. ISBN: 978-84-16325-89-4. 22-25. Open access. http://hdl.handle.net/10317/7652

- Álvarez-Hernández, M.H., Martínez-Hernández, G.B., Castillejo, N., Martínez, J.A., Artés-Hernández, F. 2021. Antifungal activity of a thymol-based active packaging system for tomato preservation. In F. Artés-Hernández, J.A. Fernández-Hernández, R. Zornoza, M.D. de Miguel, J.J Alarcón, J.E. Cos, J.M. Molina (Eds.). Proceedings of the 9th Workshop on Agri-Food Research for young researchers. CRAI Biblioteca, Universidad Politécnica de Cartagena, Cartagena, Murcia, Spain. ISBN: 978-84-17853-29-7. 23-26 pp. Open access http://hdl.handle.net/10317/9241

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- Álvarez-Hernández, M.H., Martínez-Hernández, G.B., Castillejo, N., Martínez, J.A., Artés-Hernández, F. 2021. Effect of an active packaging containing an ethylene scavenger and thymol on fungal development and quality changes of cherry tomatoes.

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