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Efficacy of photocatalysis and photolysis systems for the removal of ethylene under different storage conditions

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ABSTRACT

Most fresh horticultural commodities are highly perishable and ethylene often plays an important role in their ripening and senescence process. Reduction of ethylene concentrations around these commodities may lead to the slowing down of metabolic processes, which could potentially extend their storage or shelf life. The objective of this work was to investigate photocatalytic oxidation (PCO) and vacuum ultraviolet light (VUV) photolysis for ethylene removal in fruit storage. The efficacy of both techniques for ethylene removal was analyzed under different storage conditions (initial ethylene concentration, oxygen, relative humidity and temperature). Ethylene removal in VUV photolysis was much faster than PCO with the reaction mechanism followed by Langmuir-Hinshelwood and first-order equations, respectively. Higher O_2 concentration in the reactor favored both ethylene removal processes. However, high relative humidity impeded PCO and enhanced VUV photolysis efficacy of ethylene oxidation. Lowering the temperature from 21 °C to 1 °C showed no consistent trend of temperature effects on ethylene removal in the PCO process, whereas in VUV photolysis, reducing the temperature decreased ethylene removal significantly ($p \leq 0.05$). Ethylene removal in a gas stream with a single pass through VUV photolysis reactor was 84.8% whereas it was only 14.9% in PCO reactor. Apple storage revealed that the ethylene concentration increased to 70 $\mu L\,L^{-1}$ in 8 days at 1 °C. This concentration was brought down to 24 and 2.6 $\mu L\,L^{-1}$ in storage chambers connected to PCO and VUV reactors, respectively. Further research efforts are needed to improve the performance of the reactors for the complete removal of ethylene in postharvest storage of fresh produce.

1. Introduction

Most fresh fruit and vegetables are highly perishable commodities and for the products to reach the consumer in good quality it is often essential to slow down ethylene-induced ripening in the supply chain. Ethylene has been known to play a pivotal role in accelerating ripening and senescence in fresh produce (Saltveit, 1999). The benefits of reducing ethylene levels in slowing down ripening and senescence, and increase in shelf life of some climacteric and non-climacteric horticultural commodities have been widely studied (Ku et al., 1999; Wills et al., 2001; Pathak et al., 2017c). Therefore, ethylene management is of importance along the supply chain. Generally, most fruit handling companies and storage facilities rely on various traditional methods such as air ventilation, the use of ethylene adsorbers and oxidizers, or the use of air filtration equipment based on catalytic oxidation/ photocatalysis and ozone generators (Wills, 2015; Martínez-Romero et al., 2007; Zagory, 1995).

The suitability of a method for ethylene management depends on the type of storage and product. For instance, in packaged fresh produce ethylene adsorbent/absorbent-packages, -sachets, -sheets and/or -pads could be used. These materials may include, potassium permanganate, activated carbons, clay, zeolite and palladium based scrubbing material (Álvarez-Hernández et al., 2018; Terry et al., 2007). They suffer limitations in terms of the absorption/adsorption capacity as over time they may get saturated and require replacement, which may not be ideal in case of long-term storage and distant shipping (Martínez-Romero et al., 2007; Pathak et al., 2017a). Air ventilation can be an inexpensive technique, however, it is not suitable for all regions due to unsuitable environmental conditions and cannot be applied in case of controlled atmosphere storage (Thompson, 1998). For continuous ethylene removal in closed storage units there are equipment available, such as, ozone generators and filtration units based on catalytic

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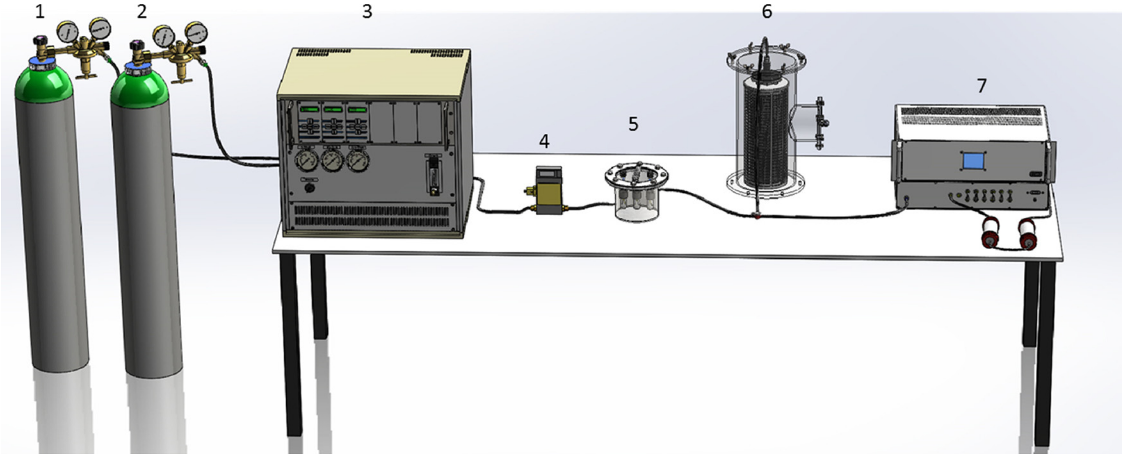


Fig. 1. Schematic of the experimental setup used for studying ethylene removal in photocatalytic (PCO) and photolysis (VUV) reactor. 1 - Synthetic air cylinder, 2 - ethylene cylinder, 3 - Gas mixer, 4 - Flow controller, 5 - Reactor (PCO/VUV), 6 - Activated carbon for ozone absorption (only in case of VUV reactor), 7 - Ethylene detector.

oxidation/photocatalysis (Keller et al., 2013; Martínez-Romero et al., 2009). In usage of ozone generators, it is important to control ozone concentrations, as ozone is hazardous to human health and recommended exposure limit is 0.1 μL L^{-1} for 8 h by United States occupational safety and health administration (US-OSHA). Similarly, high concentrations of ozone can also cause injury in plant tissues (Smilanick, 2003). The catalytic oxidation based filters require high temperatures as oxidation of ethylene occurs at temperatures above 100 °C (El Blidi et al., 1993).

Photocatalytic oxidation (PCO) is another technique that can be used for ethylene removal. It is based on the use of ultraviolet light and catalysts, such as titanium dioxide (TiO_2), which is most popularly used. The technique can be described in principle as a 'green' technique as it does not leave behind any residue (Gonzalez et al., 1999). Ethylene is oxidized into carbon dioxide (CO_2) and water in a complete oxidation reaction. The application of photocatalytic oxidation has been widely studied for the removal of volatile organic compounds in gaseous as well as aqueous state (Ibhadon and Fitzpatrick, 2013). There is also an emerging research on development of PCO for ethylene removal in fruit and vegetables storage rooms (Maneerat and Hayata, 2006; de Chiara et al., 2015; Hussain et al., 2011a; Nielsen et al., 2015). Another technique reported in literature for removal of ethylene is vacuum ultraviolet light photolysis (VUV), which is based on the use of shortwave (≈185 nm) UV irradiation. The potential of this technique to oxidize ethylene has been demonstrated using lab scale reactors (Pathak et al., 2017b, c; Scott and Wills, 1973). The lab scale reactor developed by Pathak et al. (2017b) displayed an ethylene removal efficiency of 76% in a flow through system in which 5 μL L^{-1} ethylene concentration was supplied at a flow rate of 0.5 L min^{-1}. Additionally, the reactor was able to reduce ethylene concentration to 1.8 μL L^{-1} inside a storage chamber consisting of mixed fruits (apple, banana, kiwifruit) stored at 15 °C for 10 d, while under same conditions the control storage chamber had 90 μL L^{-1} of ethylene accumulation (Pathak et al., 2017c).

Both PCO and VUV photolysis have some similarities in the working principles as reactive oxygen species (ROS) are generated in both techniques that eventually oxidize ethylene. In PCO, on irradiation with ultraviolet light electron-hole pair generation takes place on the catalyst surface that react with surface adsorbed oxygen and water molecules to produce ROS. On the other hand, in VUV photolysis, oxygen and water molecules in gaseous state are dissociated under VUV irradiation to produce reactive oxygen species, In spite of the similarities, the overall working and efficiency of both processes in oxidation of gaseous impurities is different (Jiang et al., 2015). The objectives of this study were to investigate the efficacy (the performance) of the two techniques (PCO and VUV photolysis) in terms of the amount and rate of ethylene removal; and to assess their potential for application in actual fruit storage. To understand the ethylene removal efficiency of these two techniques, experiments were conducted at varying ethylene concentrations 2 μL L^{-1} to 35 μL L^{-1} and the kinetics of the two techniques was analyzed.

In addition, storage of fruit and vegetable requires optimum refrigerated conditions, modified or controlled atmosphere with low O_2 and/or high CO_2, which are well established and commercially adopted (Watkins, 2016; Gross et al., 2016). These conditions involve low temperature, high relative humidity (RH), low O_2 and high CO_2 atmospheres, which vary depending on the type and condition of fresh produce. Thus, for application of ethylene removal techniques in fruit storage, it is important to evaluate the performance of the ethylene removal techniques under similar storage conditions. Hence, another objective in this study was to investigate the efficiency of PCO and VUV photolysis in the removal of ethylene under different storage conditions: temperatures (0, 6, 14, and 21 °C), and O_2 concentrations (low and high) and RH (low and high). A case study experiment based on the application of PCO and VUV photolysis techniques to assess ethylene removal in apple storage at 1 °C was also conducted.

2. Materials and method

2.1. Photocatalytic and photolysis reactor

Two steel reactors (diameter 12 cm, height = 11 cm each) developed in-house (Fig. 1), were used to carry out the experiments for PCO and VUV photolysis experiments, respectively. The PCO reactor consisted of three UV lamps (3 W each) irradiating at 254 nm and TiO_2-coated glass slides, while, the VUV photolysis reactor consisted of three UV lamps (3 W each) with irradiation at 254 nm and also a small percent at 185 nm. Lamps were supplied by Dinies (Germany). No TiO_2-coated plates were used for VUV photolysis. The lid of both reactors was provided with a rubber septum for gas sampling and electrical fittings for the UV lamps as well as temperature and humidity sensors (FHA 646-R, Ahlborn, Holzkirchen, Germany). The instrumental error of sensors is ± 0.1 K for temperature, and ± 2% for relative humidity. To enable flushing of the reactor with a gas of desired concentration, inlet and outlet ports were provided on diagonally opposite sides of the reactor.

2.2. Optimizing TiO_2 coated area

To carry out the PCO reactions, titanium dioxide (TiO_2) Degussa

P25 based FN3 solution (Advanced Materials, Kamenne Zehrovice, Czech Republic) was used as a catalyst. Titanium dioxide was chosen as a photocatalyst as it is a low cost, stable, and biologically and chemically inert (Nakata et al., 2012). Glass slides (76 × 26 mm) were used as a support for TiO_2 as glass is low cost and inert. Glass slides were dipped into FN3 solution and then dried in an oven at 50 °C for 1 h. The procedure was repeated one more time to obtain a two-layered coating on the glass slides. Advantages of coating the catalyst onto a support are better light distribution and reduction in hydrodynamic pressure problems which may arise in using unsupported particulate catalyst (Zorn et al., 2000; de Chiara et al., 2014). To optimize the TiO_2 coated area in PCO reactions, experiments were performed in a closed steel reactor with fixed initial ethylene concentration ($5\,\mu L\,L^{-1}$) and varying surface areas of TiO_2, 59.3, 177.8 and $296.4\,cm^2$, obtained by changing the number of TiO_2-coated glass slides (cm^2/slide). Lamps were switched on once stable initial ethylene concentration inside the reactor was attained. To avoid any discrepancy in the results due to possible catalyst deactivation only freshly TiO_2-coated glass slides were used in subsequent experiments.

2.3. *Experiments at different initial ethylene concentrations*

Ethylene production rates in fresh produce varies greatly and may range from very high ($> 100\,\mu L\ kg^{-1}\ h^{-1}$) in passion fruit; high ($10–100\,\mu L\ kg^{-1}\ h^{-1}$) in apples, pear, avocado; intermediate ($1–10\,\mu L\ kg^{-1}\ h^{-1}$) in bananas, fig, tomato; low ($< 10\,\mu L\ kg^{-1}\ h^{-1}$) in strawberries to very low ($< 1\,\mu L\ kg^{-1}\ h^{-1}$) in carrots and citrus fruits (Blanke, 2014; Saltveit, 1999). Thus, ethylene accumulation inside a closed storage chamber may vary depending on the type and amount of product, storage conditions and on the dimensions of the storage room. Therefore, the performance of the two ethylene removal processes was studied at different initial ethylene concentrations (2, 5, 10, 22, $35\,\mu L\,L^{-1}$) at room temperature (21 °C) and RH < 10%. A static system (closed reactor) was used and the PCO and VUV photolysis were carried out simultaneously in two different reactors. Before carrying out any experiment, the reactors (with or without TiO_2-coated glass plates) were flushed for 20 min with compressed air ($20.5 \pm 0.5\%$ O_2 in N_2, Air Liquide, Berlin, Germany) to remove any impurities or gaseous products remaining from previous experiments.

In order to create different initial ethylene concentrations, calculated amount of ethylene with a concentration of 10 and $100\,\mu L\,L^{-1}$ was injected into the reactors using a syringe of 5 mL capacity. Ethylene concentration was verified by drawing gas samples (5 mL) from the rubber septum provided in the lid of the reactor. A photoacoustic system based ethylene detector, ETD-300 (Sensor sense, Nijmegen, The Netherlands), which has a detection limit of $0.3\,nL\ L^{-1}$ with a time resolution of 5 s, was used for analyzing the gas samples for ethylene measurements. The ethylene detector was operated in sample mode under a continuous supply of air flow at a flowrate of $0.04\,L\ min^{-1}$. When the ethylene concentration reached equilibrium inside the reactor, the lamps were switched on. Ethylene concentration were measured at regular intervals till the concentration decreased to $< 0.04\,\mu L\,L^{-1}$.

2.4. *Kinetics*

2.4.1. *Photocatalytic oxidation (PCO)*

In PCO kinetic studies, Langmuir-Hinshelwood (L-H) equations are widely accepted(Yamazaki et al., 1999; Ibhadon et al., 2007) as they encompass various steps in a PCO process including absorption of the compound on the catalyst surface (Debono et al., 2017). In a basic L-H equation the reaction rate (R) is proportional to the surface coverage by the reactant, θ (Ibhadon et al., 2007) and R is a function of initial concentration of reactant (C) as described in equation below:

$$R = \frac{dC}{dt} = k\theta = \frac{k\,KC}{1 + KC} \tag{1}$$

where k is the reaction rate constant (min^{-1}), K is the adsorption coefficient of the reactant ($\mu L\ L^{-1}$) and C is the reactant concentration ($\mu L\ L^{-1}$) and t is time (min). When reactant concentration is low, the term KC can be neglected and Eq. (1) can be described as a pseudo first order reaction as shown below:

$$\mathrm{R = k'C} \tag{2}$$

where k' is the apparent first order kinetic constant (min^{-1}). It is the rate constant for pseudo first order reaction to describe later part of the ethylene degradation curves when ethylene concentration becomes very small (Batault et al., 2017). Few studies have reported PCO reactions following pseudo first order kinetics (Ye et al., 2013; Batault et al., 2017). Ethylene oxidation using a plasma photocatalytic process was described as a first order reaction by Ye et al. (2013). Contrastingly, Batault et al. (2017) reported a good fit of L-H equation for PCO degradation of toluene compared to first order kinetics. The following analytical solution to Eq. (1), obtained by integrating Eq. (1) was used in their study for fitting experimental data.

$$t = A.\left[B(C - C_0) + ln\frac{C}{C_0}\right] \tag{3}$$

where C_0 is initial ethylene concentration ($\mu L\ L^{-1}$), and A (min) and B ($\mu L\ L^{-1})^{-1}$ are kinetic descriptors.

Eq. (3) relates the time t (min) needed for the reactant degradation to the concentration C ($\mu L\ L^{-1}$). In the present study, the ethylene degradation data was fitted to L-H equation using the same analytical solution Eq. (3). The constants, C_0, A and B were estimated from the least squares regression fitting (Solver function, Microsoft Excel) and are shown in Table 1.

From the estimated values (C_0, A and B*), the* initial reaction rate (R_0) and the apparent first order kinetic constant (k') were calculated. As initial reaction rate is the instantaneous reaction rate at the start of the reaction (t = 0), R_0 ($\mu L\ L^{-1}\ min^{-1}$) was determined at t = 0 and C = C_0 using Eq. (4).

$$R_0 = -\frac{1}{A}\cdot\frac{C_0}{1 + B.\,C_0} \tag{4}$$

When concentration becomes very low, term ($B.C_0$) in Eq. (4) can be neglected, thus

$$R_0 = -\frac{1}{A}\cdot C_0 \tag{5}$$

The above equation becomes a first order reaction which can be represented by the general equation Eq. (2). Comparing Eqs. (2) and (5), k' (min^{-1}), the apparent first order kinetic constant, is calculated as $-1/A$.

Table 1
Reaction kinetic descriptors of the Langmuir-Hinshelwood model applied to photocatalytic oxidation (PCO).

Initial ethylene concentration, C_0 ($\mu L\ L^{-1}$)	Estimated coefficients and reaction rates[a]			
	A (min)	B ($\mu L\ L^{-1})^{-1}$	R_0 ($\mu L\ L^{-1}\ min^{-1}$)	K' (min^{-1})
2.1	−7.28	0.44	0.15	0.14
6.6	−7.64	0.18	0.38	0.13
11.2	−16.68	0.02	0.55	0.06
22.3	−7.73	0.04	1.53	0.13
36.6	−50.00	−0.02	4.53	0.02

[a] A and B: Kinetic constants; R_0: Initial reaction rate; K': Apparent first order kinetic constant.

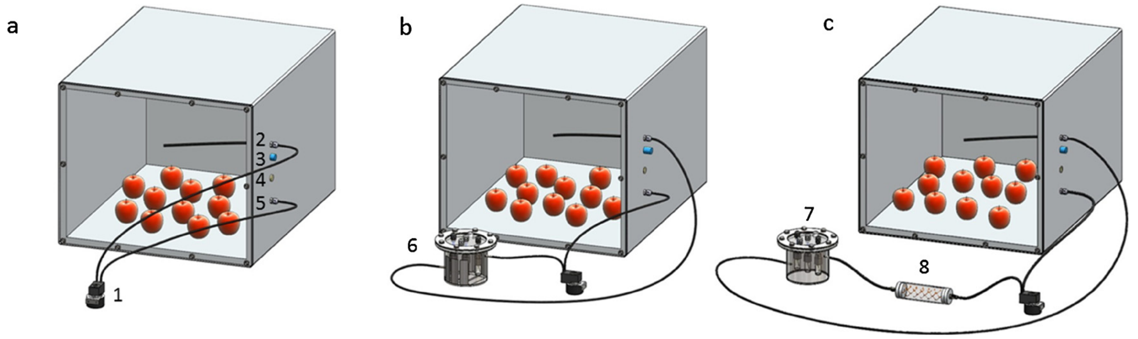


Fig. 2. Experimental setup for fruit storage. a) Control chamber, b) Photocatalytic oxidation (PCO) chamber, c) Vacuum ultraviolet light (VUV) photolysis chamber. 1- pump, 2 -inlet, 3 - temperature/humidity sensors, 4 -rubber septum, 5 -outlet,6 - PCO reactor, 7 - VUV photolysis reactor and 8-ozone filter.

2.4.2. *Vacuum ultraviolet light (VUV) photolysis*

Primary photolysis has been generally found to follow the first order kinetics (Feiyan et al., 2002) and was described by the following equation;

$$C = C_0e^{-kt} \tag{6}$$

where C is reactant concentration (μL L^{-1}) at any time (t, min), C_0 is initial concentration (μL L^{-1}), and, k is first order reaction constant (min^{-1}). The ethylene degradation curves were fitted to first order equation using Eq. (6) and k was determined using solver function in Microsoft excel. Initial reaction rate, R_0 (μL L^{-1} min^{-1}) was determined by integrating Eq. (6) at initial conditions, $C = C_0$ and $t = 0$.

$$R_0 = kC_0 \tag{7}$$

2.5. *Experiments at different storage conditions*

First set of experiments were aimed at understanding the role of different storage temperature (0, 6, 14, and 21 °C) and duration of irradiation time on the efficacy of the PCO and VUV techniques. These experiments were conducted simultaneously in the PCO and VUV photolysis batch reactors. The experimental procedure followed was similar to as described in Section 2.3. The initial ethylene concentration injected into the reactors was fixed at 10 μL L^{-1}.The temperature was varied (0, 6, 14, and 21 °C) whereas RH and O_2 concentration were kept constant at 10% and 21%, respectively. The RH and temperature inside the reactor was monitored over time using data logger specifications given in Section 2.1.

The second sets of experiments were conducted to determine the effects of RH and O_2 concentrations. The experimental conditions were RH [low (10.7 ± 1.8%)/ high (84.9 ± 6%)] and O_2 concentration [low (0.67 ± 0.16%)/ high (20.8 ± 0.08%)] at 21 °C. All experiments were conducted inside a temperature controlled room and at fixed initial ethylene concentration of 10 μL L^{-1}. Both reactors (PCO and VUV) were initially flushed with a gas of desired O_2 concentration obtained by mixing nitrogen (99%) and compressed air (20.5 ± 0.5% O_2) supplied by Air liquid, Berlin Germany. The mixed gas stream was passed through water or silica gel before entering the reactor in order to get desired RH levels. After obtaining desired RH and O_2 concentration, the inlet and the outlet of the reactors were closed and further procedure similar to Section 2.3 was followed. O_2 concentrations were measured using a gas analyser (Checkmate 3, PBI Dansensor, Ringsted, Denmark). For the second set of experiments, half time of the reaction was determined based on data obtained from continuous measurements. Half time of the reaction is described as the time taken for a reaction to reach half completion i.e. for the initial reactant concentration to reduce to 50% was determined (Wharton and Szawelski, 1982).

2.6. *Experiments with PCO and VUV reactors in actual storage chamber*

2.6.1. *Single pass – flow through system*

Prior to testing the reactors in an actual storage, the amount of ethylene removed in a single pass through the reactor was experimentally measured. An annotated diagram of the experimental setup that was used for this investigation is shown in Fig. 1. Air with desired ethylene concentration was continuously flushed (0.24 L min^{-1}) through the reactor. The desired ethylene concentration was obtained by mixing ethylene from ethylene standard, 9.88 ± 0.20 μL L^{-1} or 105.3 ± 2.1 μL L^{-1} and rest synthetic air (Air Liquide, Berlin, Germany)

The ethylene concentrations at the outlet of the reactor were continuously measured using ETD-300 (in continuous mode) and recorded. Once a stable ethylene concentration was established at the outlet, the lamps were switched on. The percentage ethylene removal (PER) was calculated as percentage of the initial stable ethylene concentration, C_i (before switching on the lamps) and final stable ethylene concentration, C_e (after switching on the lamps).

$$PER = \frac{C_i - C_e}{C_i} \times 100 \tag{8}$$

2.6.2. *Storage chamber test with apples*

Storage with apples was carried out for a short storage period of 8 d to evaluate the effectiveness of PCO and VUV ethylene removal processes. Storage experiments were carried out using air-tight chambers (190 L each) housed in a walk-in cold room set at 1 °C. Apples ‘Gala’ harvested from the experimental farm (Marquart, Potsdam, Germany) were stored inside each of the chambers (6 kg per chamber). The VUV and PCO reactors were connected separately to two of the storage chambers via pre-fitted inlets, while the third chamber served as control. The storage chamber connected to PCO is hereafter referred to as PCO chamber while the chamber connected to VUV reactor is referred to as VUV chamber. A schematic of reactors connected to the respective storage chambers is shown in Fig. 2. All chambers had an external pump connecting the inlet and outlet of the chamber to make a closed air circulation loop in each chamber. Another inlet was fitted with a rubber septum to facilitate air sampling for ethylene, O_2 and CO_2 measurements. O_2 and CO_2 concentrations were regularly monitored using a gas analyser (Checkmate 3, PBI Dansensor, Ringsted, Denmark) throughout the storage period. The pressure differences due to temperature fluctuations and sampling of air was not taken into account.

Respiration rate (RR) and ethylene production rate were measured at 1 °C and under normal atmospheric conditions before and after storage of fruits using a closed system. Other quality aspects were not measured, because of short storage period and focus was on ethylene removal. RR was measured using an in-house developed respirometer consisting of 9 acrylic glass cuvettes (Rux et al., 2017). Each cuvette consists of a non-dispersive infra-red CO_2 sensor (GMP222, Vaisala

GmbH, Bonn, Germany), with a measuring capacity up to 5000 μL L^{-1} of CO_2. Twelve apples were randomly selected from each storage chamber and distributed equally in three cuvettes. CO_2 production was recorded over a period of six hours and RR was calculated and expressed in nmol kg^{-1} s^{-1}.

For ethylene production rate, nine apples were randomly selected from each storage treatment chamber, and divided into batches (three apples per batch). Each batch was placed inside hermetically sealed small steel chambers (2.5 L). Air samples from the chambers were periodically drawn using a syringe from the rubber septum provided on top of the lid of chambers and analyzed for ethylene concentration. Ethylene production rate was calculated as the amount of ethylene produced per unit time per unit mass of the fruit (nmol kg^{-1} s^{-1}).

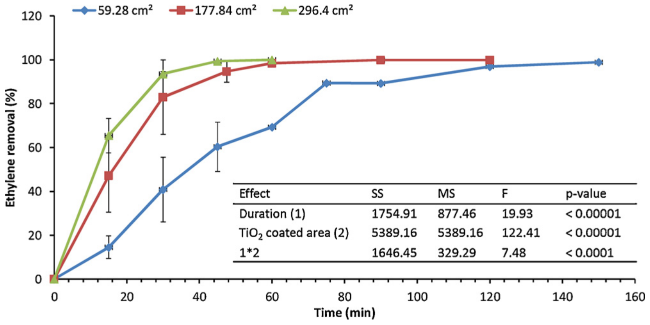
2.7. Statistical analysis

Factorial experimental designs were used in this study. The effects of total surface area exposed to TiO_2 and duration (exposure time or the irradiation time), and of their interactions were investigated on ethylene removal (%). In another experimental setup, the efficacy of ethylene removal systems as function of the storage temperature (0, 6, 14, and 21 °C) and duration was investigated using normalized ethylene concentration. Furthermore, the efficiency of ethylene removal the two systems was investigated as function of the storage humidity, and oxygen concentration and of their interactions at a constant temperature 21 °C. Data obtained were subjected to factorial analysis of variance (ANOVA) using Statistical software (Statistica 10.0, StatSoft Inc., Tulsa, OK, USA). Fisher Least significant differences test was used to test the statistical significant differences at $p \leq 0.05$. All the results obtained were presented as mean (n = 4 or n = 3 depending on the experimental setup) ± standard deviation (SD).

3. Results and discussion

3.1. Effect of titanium dioxide surface area on PCO

The individual factors (TiO_2 coated surface area and the duration of exposure or the irradiation time) and their interactions were found to have a significant impact ($p \leq 0.05$) on percentage ethylene removal (Fig. 3). In all PCO experiments conducted with 5 μL L^{-1} initial ethylene concentration using different TiO_2-coated area, ethylene removal percentage was ≥99.9%. However, the time required for ≥99.9% ethylene removal was dependent on the exposed surface area of TiO_2. It took 150, 120 and 60 min for ethylene removal to reach to ≥99.9% in the PCO reactor with 59.3, 177.8 and 296.4 cm^2 TiO_2 coated area, respectively. A continuous reduction in ethylene concentration was observed over time, and, higher the TiO_2-coated surface area the faster was ethylene oxidation rate. These results are consistent with literature as Chang et al. (2013) in their experiments involving photocatalyst, reported an increase in percentage removal of ethylene from 22.4% to 39% on increasing TiO_2 area inside the reactor from 83.4 to 259 cm^2.



Effect	SS	MS	F	p-value
Duration (1)	1754.91	877.46	19.93	< 0.00001
TiO_2 coated area (2)	5389.16	5389.16	122.41	< 0.00001
1*2	1646.45	329.29	7.48	< 0.0001

Fig. 3. Effect of titanium dioxide coated area on percentage ethylene removal. Error bars indicate standard deviation from mean values (n = 4).

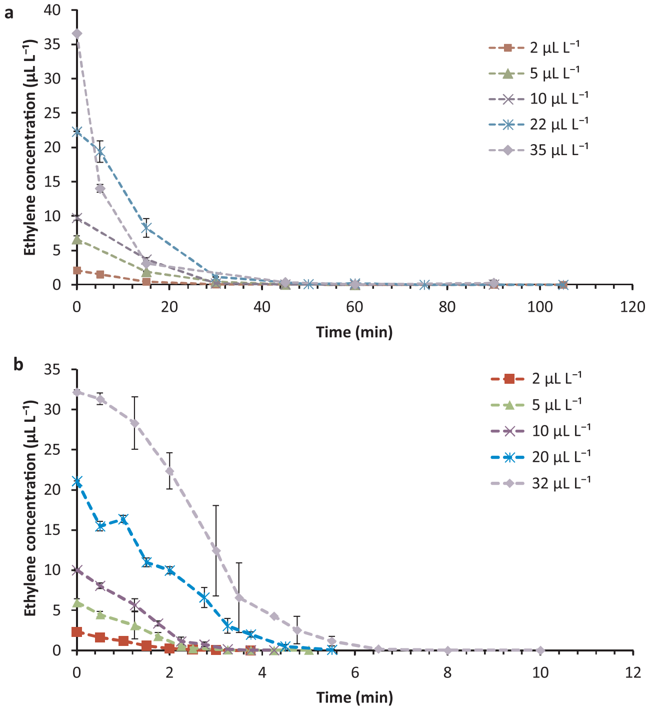


Fig. 4. Ethylene concentration as a function of irradiation time a) Photocatalytic oxidation (PCO) and b) Vacuum ultraviolet photolysis (VUV). The legends denote different initial ethylene concentration. Error bars indicate standard deviation from mean values (n = 3).

Photocatalysis is a surface dependent phenomenon and the surface area of the catalyst exposed to the radiation influences ethylene oxidation (Chang et al., 2013; Tytgat et al., 2012). According to Ibhadon and Fitzpatrick (2013) photocatalytic process involves diffusion and adsorption of reactant to the surface of semiconductor, reaction on the surface of semiconductor and subsequent desorption and diffusion of the products from the surface of the semiconductor. Thus, the more the UV irradiated TiO_2-coated surface area, the greater is the ethylene removal. Therefore, further study was conducted using 296.4 cm^2 of TiO_2-coated surface area.

3.2. Effect of ethylene concentration and kinetics of ethylene degradation

Ethylene concentration as a function of time is presented in Fig. 4. The initial maximum ethylene concentrations of 35 μL L^{-1} and 32 μL L^{-1} were reduced to < 0.04 μL L^{-1} within < 50 min and < 7 min in PCO and VUV processes, respectively. It was evident that the VUV technique was much faster compared to PCO process. This was due to the fact that VUV technique relies on ethylene oxidation in the gaseous phase whereas; PCO is a surface phenomenon, which mainly occurs at the irradiated surface of the photocatalyst (Huang et al., 2011). Comparing two processes for toluene removal, Huang et al. (2011) reported a much higher toluene removal efficiency for VUV photolysis (63.9%) compared to PCO (14.3%) at a flow rate 1 L min^{-1} and initial toluene concentration 50 μL L^{-1}. Further in this study, the reaction kinetics of the two processes was investigated separately.

3.2.1. Photocatalytic oxidation (PCO)

A very good degree of fit was obtained ($R^2 > 99\%$) on fitting ethylene degradation curve to L-H equation (Eq. (3)).

The calculated initial reaction rate (R_0) (using Eq. (4)) was found to be dependent on the initial ethylene concentration. A lower reaction rate was obtained at low ethylene concentrations. In PCO studies, the reaction rate has been found to be dependent on the initial reactant concentration. Yamazaki et al. (1999) observed that the PCO reaction rate follows L-H kinetics with respect to ethylene concentration and reported a linear relationship between the reciprocal of reaction rate and that of initial ethylene concentration. In other related studies, increasing reaction rate with inlet ethylene concentration was reported to stabilize/decrease after a certain threshold ethylene concentration is reached. In a study of ethylene photocatalytic oxidation using C-doped TiO_2, Lin et al. (2014a) observed an increase in reaction rate on increasing ethylene concentration from $55\,\mu L\,L^{-1}$ to $459\,\mu L\,L^{-1}$. However, the authors observed that beyond $459\,\mu L\,L^{-1}$ ethylene concentrations, the reaction rate decreased. In another similar study, using N-doped TiO_2 and increasing ethylene concentration from $100\,\mu L\,L^{-1}$ to $900\,\mu L\,L^{-1}$, reaction rate increased initially and then stabilized. This behavior can be explained on the basis of L-H kinetics (Lin et al., 2014b). In Eq. (1), it can be observed that the reaction rate (R) is proportional to the fraction of the catalyst surface (θ) covered by ethylene (Lin et al., 2014a). It is assumed that there are a limited number of active sites for ethylene adsorption on the catalyst surface. Initially at low ethylene concentrations, the number of active sites was much more with respect to that of ethylene molecules. When the ethylene concentration further increased, ethylene molecules occupied more number of active sites on the catalyst surface, resulting in a greater coverage of the catalyst surface and increased reaction rate. However, once all active sites on the catalyst surface get occupied by ethylene molecules, a further increase in ethylene concentration would no longer increase the reaction rate. According to Hay et al. (2015), this limiting ethylene concentration beyond which reaction rate stabilizes/decreases, is dependent on the light intensity, the nature of the catalyst as well as on the reactant.

3.2.2. *Vacuum ultraviolet light (VUV) photolysis*

The estimated reaction constants (k, R_0) using Eqs. (6) and (7) are shown in Table 2. The initial reaction rate showed a good first order dependence on initial ethylene concentration. In a VUV photolysis study (Chang et al., 2013), the amount of ethylene removed increased on increasing the initial ethylene concentration, at the same flow rate, that evidently showed that reaction rate increases with increase in initial ethylene concentration. Similar results were observed in degradation of formaldehyde using VUV photolysis (Yang et al., 2007). Overall, the reaction rates were higher for the VUV photolysis compared to PCO. Thus, ethylene removal using VUV photolysis can be advantageous in terms of higher efficiency.

3.3. *Ethylene degradation under different storage conditions*

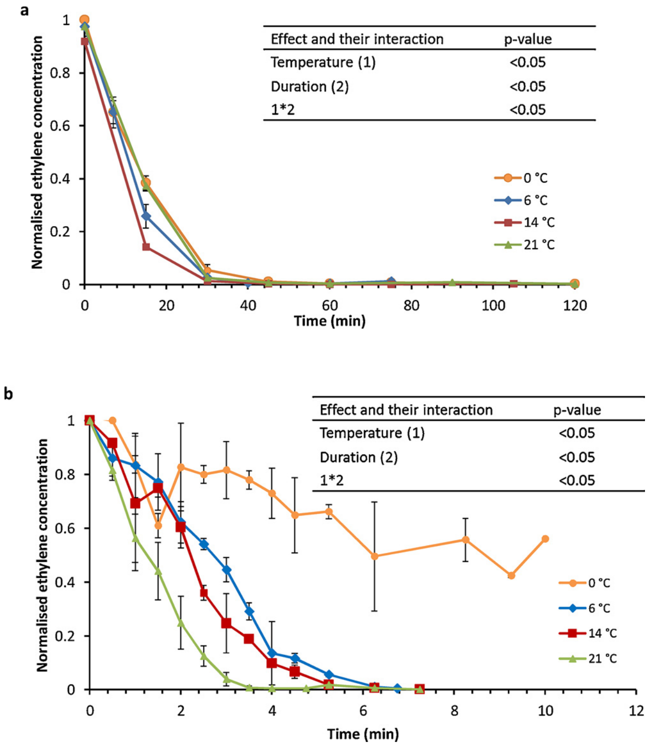
3.3.1. *Storage temperature*

Fig. 5 presents the normalized ethylene concentration (obtained by dividing the measured ethylene concentration value with that of initial ethylene concentration) with respect to temperature. From the statistical analysis, the interactive effect of temperature and duration (or irradiation time) as well as individual effects of temperature and irradiation time significantly ($p \leq 0.05$) affected percentage ethylene removal in both PCO and VUV photolysis. However, a consistent trend of the effect of temperature on ethylene removal in PCO was not observed (Fig. 5a). PCO process has been reported to be less sensitive to temperature (Mills et al., 1993) however, there are contradicting reports available in the literature (Yamazaki et al., 1999; Fu et al., 1996; Westrich et al., 2011). Ethylene oxidation was found to increase on increasing temperature from 30 to 110 °C by Fu et al. (1996). Effect of very high temperatures 65–500 °C have been reported by (Westrich et al., 2011; Yamazaki et al., 1999). Hussain et al. (2011b) also reported a slight increase in percentage ethylene removal on increasing temperature from 30 °C to 35 °C, however, at temperatures > 35 °C the percentage removal decreased. Small increase (< 10%) in ethylene oxidation was reported on increasing the temperature from 5 °C to 25 °C, by Maneerat et al. (2003). Similar effect of temperature on ethylene oxidation was reported by Obee and Hay (1997), who conducted experiments at three temperatures (2, 27 and 48 °C) and ethylene oxidation rate was found to be higher at elevated temperatures. The results and responses were attributed to the change in adsorption energies of water and ethylene molecules. At high temperatures, water is desorbed to a higher extent leaving active sites vacant for ethylene molecules to get adsorbed, thereby increasing the ethylene oxidation. In present study, similar effect of temperature could not be observed which may be due to the small range of the selected temperatures (0–21 °C)

Table 2
Reaction kinetic descriptors of the first order kinetics applied to vacuum ultraviolet light (VUV) photolysis.

Initial ethylene concentration, C_0 ($\mu L\ L^{-1}$)	Estimated coefficient and reaction rate[a]	
	K (min^{-1})	R_0 ($\mu L\ L^{-1}\ min^{-1}$)
2.3	1.02	2.05
6.0	0.88	4.38
10.0	0.88	8.80
21.1	0.47	9.36
32.2	0.47	14.14

[a] R_0: initial reaction rate; K: first order kinetic constant.



Effect and their interaction	p-value
Temperature (1)	<0.05
Duration (2)	<0.05
1*2	<0.05

Effect and their interaction	p-value
Temperature (1)	<0.05
Duration (2)	<0.05
1*2	<0.05

Fig. 5. Effect of temperature on ethylene removal in a) Photocatalytic oxidation (PCO) b) Vacuum ultraviolet photolysis (VUV). All experiments were carried out at 10% relative humidity, and 21% O_2. Error bars indicate standard deviation from mean values (n = 3). Statistical analysis on the effect and interaction is presented for percentage ethylene removal.

Under the VUV photolysis (Fig. 5b), ethylene removal was faster when temperature was higher. The ethylene concentration dropped below $< 0.02\,\mu L\,L^{-1}$ within 3.5, 5, 6.25 min at 21, 14, and 6 °C, respectively. This was in agreement with Bhowmick and Semmens (1994) who reported a small increase in reaction rate on increasing inside reactor temperature from 45 to 65 °C. In the present study, almost complete ethylene removal ($0.0007\,\mu L\,L^{-1}$) was achieved in 7.25 min at 21 °C, however, at 0 °C ethylene removal was slow and $5.6\,\mu L\,L^{-1}$ of ethylene remained at the end of 10 min. Due to its reduced efficiency at low temperature, VUV photolysis may not be as advantageous in cold

Table 3

Effects of varying oxygen concentrations, relative humidity and ethylene removal techniques (photocatalytic oxidation and vacuum ultraviolet photolysis) on the half time (min) of ethylene concentration at 21 °C.

Ethylene removal technique	Storage parameters	Half time (min)
PCO	Low RH* Low O2	27.5 ± 0.7
	Low RH* high O2	15.75 ± 1.8
	High RH* Low O2	28.75 ± 0.4
	High RH* High O2	27.25 ± 0.4
VUV	Low RH* Low O2	1.35 ± 0.1
	Low RH* high O2	1.95 ± 0.8
	High RH* Low O2	0.9 ± 0.4
	High RH* High O2	0.63 ± 0.0

Effects and their interactions	P values
Ethylene removal technique	0.000000
RH	0.000094
O_2	0.000029
Ethylene removal technique*RH	0.000012
Ethylene removal technique*O_2	0.000020
RH*O_2	0.000278
Ethylene removal technique*RH*O_2	0.000085

Mean values (n = 3) ± standard deviation of half time (min). RH: relative humidity - low (10.7 ± 1.8%); high (84.9 ± 6%), and O_2 concentration - low (0.67 ± 0.16%); high (20.8 ± 0.08%). Initial ethylene concentration of 10 μL L^{-1}.

storages as in higher temperatures storage (> 13 °C) of tropical fruits. However, investigation of up-scaled VUV photolysis reactor system is recommended to confirm this observation.

3.3.2. *Oxygen concentration and relative humidity*

Individual factors O_2 concentration, relative humidity and the type of ethylene technique (PCO and VUV photolysis) and their interactions had a significant impact ($p \leq 0.05$) on total ethylene removed. Table 3 presents the half-time of the ethylene oxidation under different O_2 and RH conditions in PCO and VUV photolysis reactors, respectively. A smaller half-time indicates a faster reaction. Relative humidity and O_2 clearly showed an effect on half-time of both the processes. The PCO reactor had the shortest half-time, and, the fastest ethylene removal was observed at higher O_2 concentration and low RH (Table 3). Higher O_2 has been reported to have a beneficial effect on photocatalytic oxidation (Lin et al., 2014a, b). On the other hand, high RH was unfavorable for PCO as it was evident that in both O_2 concentrations (low O_2 and high O_2) with high RH the reaction was found to be slower than that of low RH. This is in agreement with Tytgat et al. (2012) and Obee and Hay (1997) who reported negative impact of RH on ethylene oxidation. In contrast, other studies reported that a small quantity of water vapor favored oxidation efficiency of ethylene in PCO (Hussain et al., 2011b; Park et al., 1999; Westrich et al., 2011). In photocatalysis, the trapping of electron-hole pairs is by surface adsorption of O_2 and water molecules on the surface that leads to the formation of hydroxyl radicals and superoxide ions. These reactive oxygen species (ROS) then oxidize the ethylene on the catalyst surface. Thus, in theory, the presence of water vapor and O_2 should produce more ROS, which should to lead to higher ethylene removal. However, presence of water molecules may not necessarily lead to increased ethylene removal efficacy as both water vapor and ethylene molecules compete for the same adsorption sites on the catalyst surface (Yamazaki et al., 1999). Although excess accumulation of water vapor may produce more ROS but water molecules equally compete with ethylene molecules for adsorption onto the active sites on catalysts surface. Water having higher absorption affinity limits the number of active sites for ethylene adsorption, consequently, decreasing the ethylene oxidation in PCO (Obee and Hay, 1997). Furthermore, the active sites for O_2 adsorption are separate hence O_2 concentration does not interfere with ethylene adsorption, and thus presence of O_2 favor PCO process. This was evident from Table 3 that higher ethylene removal occurred at high O_2 concentration and low RH. Thus, the application of this PCO system could be limited under cold storage since high relative humidity is required, however, investigation of up-scaled PCO reactor system is recommended to confirm this observation.

In the case of VUV photolysis, the favorable impact of RH on ethylene oxidation was observed (Table 3). Lower half-time was obtained at high RH conditions compared to low RH conditions. This is agreement with literature that presence of water enhances the VUV photolysis of ethylene (Chang et al., 2013; Jeong et al., 2004). Moreover, since no catalyst is involved, there is no competing adsorption effect as in PCO. The lowest half-time was achieved at high O_2 concentration and high RH (Table 3). Both, water vapor and O_2 molecules absorb the photon energy to produce ROS that oxidize ethylene. As a result both high O_2 and high water vapor favor ethylene oxidation. Overall, the impact of RH was more prominent with faster reaction rate at higher RH irrespective of the O_2 concentration (Table 3). In a study by Jeong et al. (2004), oxidation of toluene under VUV photolysis increased from 10% to 91% on increasing the RH from < 1% to 40%. Chang et al. (2013) also reported increase in ethylene oxidation from 22.4 to 41.9% by increasing RH from < 1% to > 86%. It can be concluded that hydroxyl radicals are the dominant oxidizing species in VUV photolysis.

3.4. *Single pass efficiency and storage experiment*

Fig. 6 shows the difference in percentage ethylene removal (PER) in a single pass in a flow through system connected to PCO and VUV reactors. Calculated PER in VUV photolysis reactor was 84.8% whereas it was < 14.86% in PCO reactor. This difference was due to PCO being a surface process whereas VUV photolysis occurs in the gaseous medium, therefore, in VUV photolysi reaction occurs on the bulk phase and is faster whereas in PCO efficiency is limited by mass transfer to the surface of the catalyst (Yang et al., 2007). For the storage experiment with apples, change in ethylene concentration during the storage period in all three chambers is presented in Fig. 7a. Ethylene concentration in the control chamber continued to increase reaching 70 μL L^{-1} at the end of 8 d whereas it was 24 μL L^{-1} and 2.6 μL L^{-1} for PCO and VUV photolysis chambers, respectively. Compared to the ethylene accumulated in the control, the percentage ethylene reduction achieved in VUV photolysis and PCO chamber was 96.28% and 66.58% as shown in Fig. 7b. O_2 and CO_2 concentrations reached 18.9% and 1.10%, respectively in all the three chambers, at the end of 8 d from initial concentration of 20.3% and 0%, respectively. The RH was 97 ± 1%

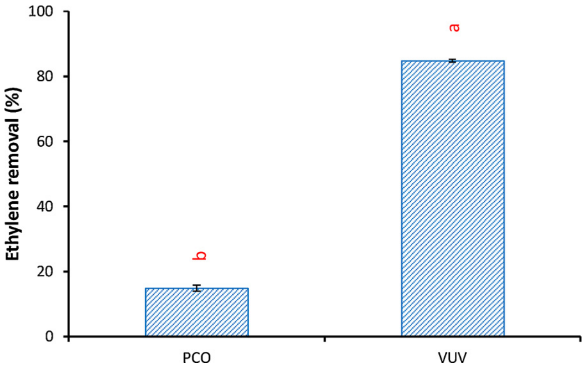


Fig. 6. Comparative percentage ethylene removal in photocatalytic oxidation (PCO) reactor and vacuum ultraviolet light (VUV) photolysis reactor in a flow through system (flowrate 0.24 L/min, initial ethylene concentration 10 μL L^{-1}). The experiments were conducted at a temperature 21 °C and relative humidity 40%. Error bars indicate standard deviation from mean values (n = 3). Different lower case letters indicate significant differences at 95% confidence interval.

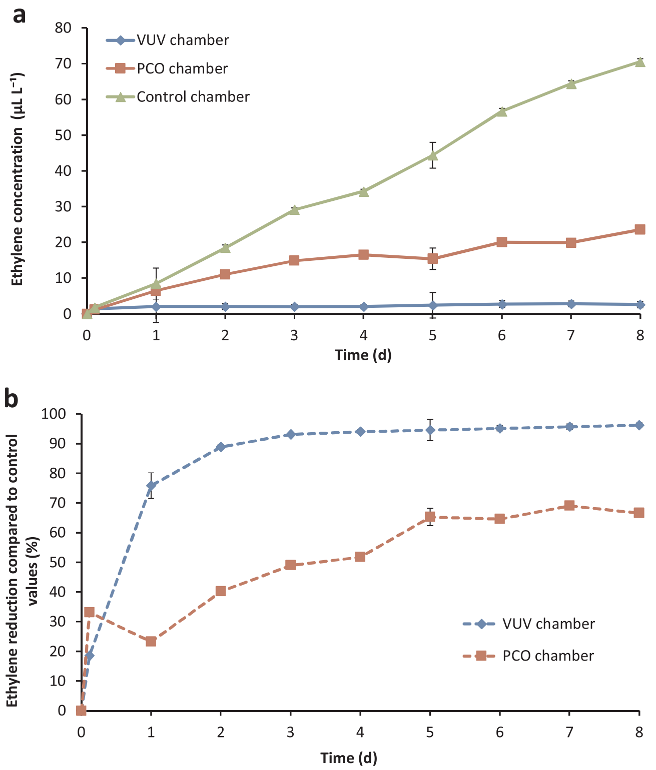


Fig. 7. (a) Ethylene concentration in different apple storage chambers stored at 1 °C during 8 d, and (b) describes the percentage ethylene reduction compared to control values. Error bars indicate standard deviation from mean values (n = 3).

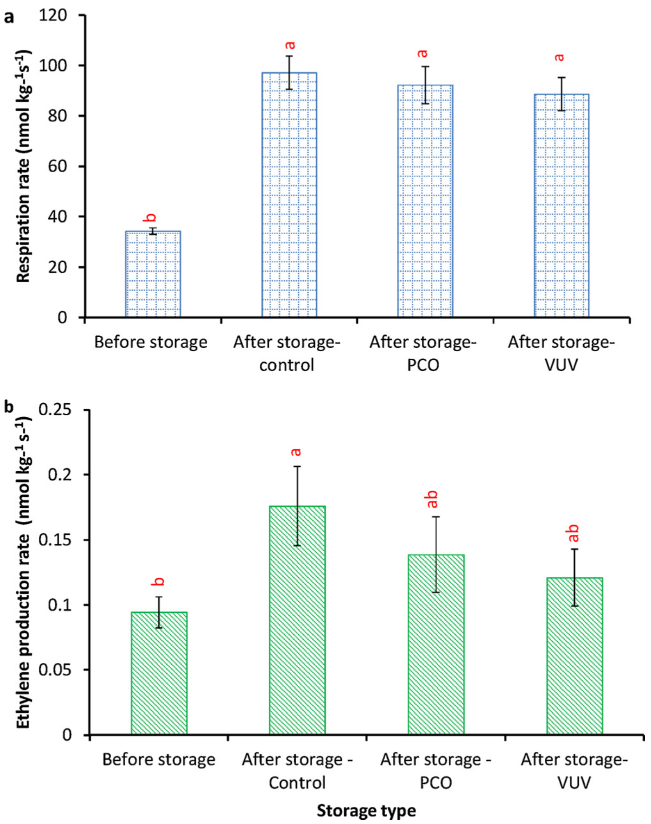


Fig. 8. Quantified respiration rate (a) and ethylene production rate (b) in apples before and after 8 day storage at 1 °C in different storage chambers. Error bars indicate standard deviation from mean values (n = 3) and bars with different letters are significantly different at 95% confidence interval.

during the 8 days.

Respiration rate (RR) and ethylene production rate, as measured before and after storage, are shown in Fig. 8. There was no significant difference in RR of apples which had been stored in the three different chambers. However, a significant increase in overall respiration rate of apples was observed after 8 d of storage compared to pre-storage which corroborates to the observations that ethylene exposure elevates respiration in many fruits and vegetables (Fugate et al., 2010; Agar et al., 1999). Furthermore, exogenous ethylene also enhances endogenous ethylene production (Park et al., 2006). The ethylene production rate of apples was significantly higher after storage for control samples compared to pre-storage. However, there were no significant differences between the pre-storage ethylene production rate and ethylene production rate after storage treatment for apples stored in PCO and VUV chambers as exogenous ethylene concentrations was less in these two chambers compared to that in control (Fig. 8b).

Both VUV and PCO reactors reduced the ethylene concentration of chambers but could not bring it down to zero even after 10 d of continuous operation of the reactor. The importance of maintaining low ethylene concentrations ($< 0.1\ \mu L\ L^{-1}$) in postharvest handling of fruits and vegetables is well known (Wills et al., 2001, 2004), thus, further research efforts are needed to improve the performance of the reactors for an effective ethylene removal in postharvest storage of fresh produce.

4. Conclusion

This study investigated two techniques namely, PCO and VUV photolysis for ethylene removal. Both techniques were able to remove ethylene and could be considered as a potential technology for application in postharvest storage of ethylene sensitive fruit and vegetables. The kinetic study of the two techniques clearly showed that both techniques were highly dependent on initial ethylene concentration with their ethylene removal efficiency being reduced at low initial ethylene concentrations. Thus, it is important to increase the efficiency of these techniques at low ethylene concentrations to avoid triggering physiological response in fresh produce. The storage parameters (oxygen concentration, humidity and temperature) were found to significantly affect the ethylene removal efficiency of PCO as well as VUV photolysis. Oxygen concentrations favored both the techniques. However, humidity impeded PCO while it enhanced VUV photolysis of ethylene. Also in VUV photolysis, the effect of humidity was dominant compared to oxygen. Temperature effect on PCO did not show any consistent trend, however, in VUV photolysis, low temperatures decreased ethylene removal efficiency. Thus, the application of VUV photolysis at low temperatures may not be fully advantageous, nevertheless, VUV photolysis has an application in storage temperature > 13 °C. In the case study experiment involving apple storage, VUV photolysis effectively lowered the ethylene concentration to $2.6\ \mu L\ L^{-1}$ compared to $24\ \mu L\ L^{-1}$ in PCO chambers, whereas in control chamber the ethylene concentration soared up to $70\ \mu L\ L^{-1}$ at the end of storage day 10. Overall VUV photolysis showed higher ethylene removal efficiency than PCO. However, an additional ozone filter coupled with VUV photolysis is needed, to prevent ozone from reaching the plant tissues and damaging them. PCO does not involve ozone generation, therefore, does not require any additional filtration mechanism. It was also observed in this study that in PCO, the higher TiO_2 surface area increased efficiency of the technique. Thus, increasing the ratio of the TiO_2 coated surface area to the volume of the reactor could effectively increase the efficiency of the process. For VUV photolysis, coupling with multifunctional catalysts (MnO_2, palladium, and cobalt) which can decompose ozone and additionally enhance ethylene degradation using the residual ozone, could be investigated. Moreover, a combination of PCO-VUV could be explored to tap the advantages of both the processes and at the same time address the individual disadvantages of the techniques.

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