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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 ($p \le 0.05$). 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 μL L^{-1} in 8 days at 1 °C. This concentration was brought down to 24 and 2.6 μL 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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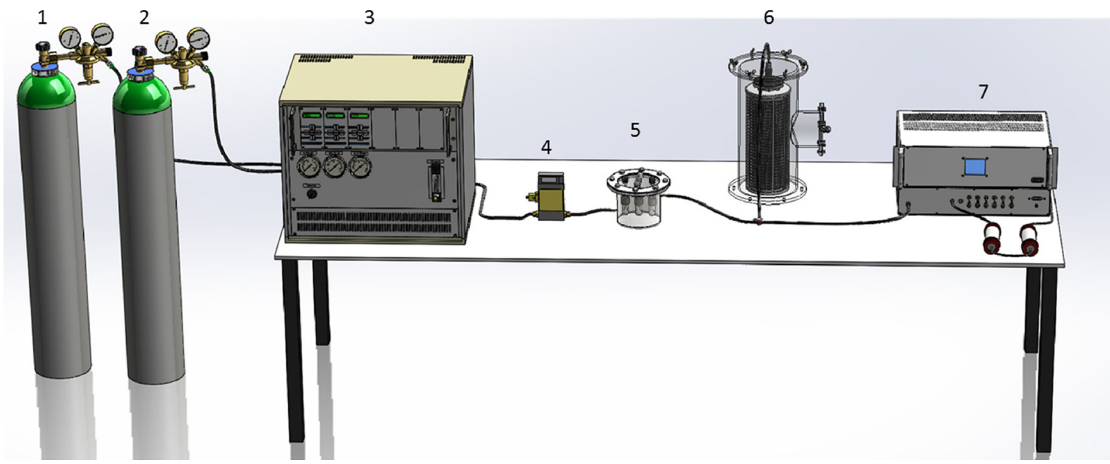

Fig. 1. Schematic of the experimental setup used for studying ethylene removal in photocatalytic (PCO) and photolysis (VUV) reactor. 1 - Synthetic air cylinder, 2 - ethylene cylinder, 3 - Gas mixer, 4 - Flow controller, 5 - Reactor (PCO/VUV), 6 - Activated carbon for ozone absorption (only in case of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