



Metal-organic frameworks have utility in adsorption and release of ethylene and 1-methylcyclopropene in fresh produce packaging



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ABSTRACT

Metal organic frameworks (MOFs) are synthetic porous materials consisting of metal ions or ion clusters bound to organic molecules to create a crystalline structure with a very high internal surface area. MOF molecules have been found to have potential utility in the selective adsorptive binding and release of gaseous fuel and other chemicals. We explored the ability of selected MOFs to bind ethylene and the ethylene action inhibitor, 1-methylcyclopropene (1-MCP) with the intent of evaluating their usefulness in regulating ethylene responses for perishable produce. We screened several MOF compounds and selected two (Basolite C300 and Basolite A520) for in-depth characterization based on their superior capacity for binding ethylene. Basolite C300 is a copper-based MOF with a trimesic acid linker group and Basolite A520 is an aluminum-based MOF with a fumaric acid linker group. Binding efficacy was compared to zeolite Z13X, which was also found to bind ethylene. The copper-based Basolite C300 was more effective at binding and retaining ethylene than the other compounds tested. When ethylene-charged sorbents were moved to dry air, they released little ethylene. However, in the presence of free water, Basolite C300 desorbed a majority of its bound ethylene. Adsorption and desorption behavior differed for other alkenes. Basolite C300 had the highest affinity for 1-MCP, but did not release bound 1-MCP in the presence of humidified air. In contrast, the compound 1-butene, often used as a surrogate to quantify 1-MCP, was bound tightly by the MOF and quickly released in the presence of humidified air. We tested the potential for in-package release of bioactive compounds from a MOF. In a proof-of-concept experiment, we found that ethylene-loaded Basolite C300 released ethylene rapidly into packages of banana fruit and induced ripening; MOF without ethylene loading did not induce ripening. The data suggest that MOFs have the potential to sorb, store, and release gaseous compounds that impact plant physiology and may have some utility as a delivery system for volatile plant growth regulators.

1. Introduction

Ethylene, a gaseous plant hormone, is endogenously produced by many plant organs. It is responsible for modifying fruit and vegetable quality and longevity by increasing metabolic rates, softening tissues, and accelerating aging, ripening and senescence (Saltveit, 1999). Reducing ethylene action can reduce postharvest losses, improve food security, and help economic sustainability. Conversely, however, increased ethylene action is sometimes desirable and a number of means of supplying exogenous ethylene have been developed (Beaudry and Kays, 1988).

High levels of CO₂ and low levels of oxygen O₂ reduce the synthesis and perception of ethylene (Burg and Burg, 1967; Abeles et al., 1992).

This relationship has been used to limit ethylene action in modified atmosphere packaging of perishables (Beaudry, 1999; Brecht et al., 2004; Kader, 1997). However, there are limits to the utility of passive MAP (Beaudry, 2000), which makes the option of active modification of the package atmosphere an attractive option. Active packaging is the intentional and dynamic modification of O₂, CO₂, ethylene, or other biologically active gas within the package through scavenging or release (Marrero and Kader, 2006). Scavenging ethylene can extend the shelf-life of packaged produce (Abe and Watada, 1991; Mehyar and Han, 2011; Zagory, 1995). Scavenging technologies use ethylene adsorbents (adsorption is the adhesion of molecules on the surface of an adsorbent, typically in a film), absorbers (absorption is the dissolution of a molecule into an absorbent), and oxidizers including potas-

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sium permanganate, activated carbon, electron-deficient diene and trienes (benzenes, pyridines, etc.), clays, and zeolites and are applied as a sachet/strip in the package or are integrated into the packaging material (Almenar et al., 2006).

Efficacy of scavengers differ, however, and performance in humid environments and be markedly reduced. Zeolite modified with palladium had a superior ethylene adsorption capacity than potassium permanganate-based scavengers when used in low amounts and is effective in scrubbing ethylene emanating from packaged produce at high relative humidity (Terry et al., 2007). A Chilean natural zeolite showed nearly double ethylene adsorption compared to a commercial Na⁺ montmorillonite (Cloisite Na⁺) and can also scavenge ethylene from the package headspace when incorporated into the packaging film (Coloma et al., 2014).

Ethylene release can be effected by a number of compounds (Beaudry and Kays, 1988) although its use in packaging environments is limited. Beaudry (1996, 1997) developed a package to be attached to the surface of a bulky plant organ and mechanically triggered to induce ethylene effects like ripening (Mir and Beaudry, 2001). Cyclodextrin and starch have the potential to act as ethylene delivery mechanisms in which the ethylene is released from adsorption surfaces by the presence of water vapor (Ho et al., 2011a,b; Ho and Bhandari, 2016; Shi et al., 2017).

The chemical 1-methylcyclopropene (1-MCP) inhibits ethylene action in plants (Sisler and Blankenship, 1996). 1-MCP is used commercially to improve storability of some perishables and is available from several suppliers. One formulation, SmartFresh (AgroFresh, Collegeville, PA, USA) consists of a sugar-based powder (cyclodextrin) that encapsulates 1-MCP and releases it once mixed with water or exposed to a humid environment (Daly and Kourelis, 2000). The release of 1-MCP from cyclodextrin can be modulated using film barriers (Mir and Beaudry, 2001; Macnish et al., 2004; Sittipod and Beaudry, 2002) or by inclusion of hygroscopic compounds in the cyclodextrin formulation (Sittipod et al., 2003).

A new class of synthetic porous materials called metal-organic frameworks (MOFs) has been developed to capture gases in fuel and chemical industries (Kuppler et al., 2009). MOFs are crystalline compounds consisting of metal ions or ion clusters bound to often-rigid organic molecules to form porous structures. The combination of organic and inorganic building blocks in a highly-ordered, porous crystalline structure offers an almost infinite number of combinations, enormous flexibility in pore size, shape and structure, and many opportunities for functionalization, grafting, and encapsulation (Li et al., 2009; Shekhah et al., 2011; Kuppler et al., 2009).

MOFs selectively adsorb and desorb many volatile molecules including ethylene and other biologically active compounds (Kuppler et al., 2009; Li et al., 2009). Moreover, MOFs have exceptionally high surface area (1000–3000 m² g⁻¹ or more) and are highly porous allowing for greater adsorptive surface area per gram than other encapsulating materials like zeolites and cyclodextrins. For zeolites, the majority of their mass is inactive aluminosilicate matrix; however, in MOF, the metal is the matrix itself, and each metal site is available. This results in a higher metal/mass ratio in MOFs than in zeolites (Morris, 2012).

MOF functionalities suggest a potential for application in MAP systems such as scavenging or releasing biologically active volatiles in packages of fresh produce. However, the use of MOFs for adsorption/

desorption of ethylene and other biologically active compounds has not yet been reported for this application. Furthermore, the effect of the N₂, O₂, CO₂, and water vapor on the sorption of biologically active molecules like ethylene by MOFs and zeolites is unknown. Thus, the aims of this study were to investigate the kinetics of ethylene adsorption and desorption by MOFs and zeolites as affected by gases and vapors relevant to produce packaging, measure the sorption and desorption of the ethylene analogue 1-butene, characterize the adsorption and desorption of 1-MCP, and evaluate the effect of ethylene desorption from a MOF on ripening of banana (*Musa* spp. L., AAA group, Cavendish subgroup, 'Valery').

2. Materials and methods

Four experiments were carried out in order to characterize and compare the adsorption/desorption capabilities of the adsorbents for ethylene, 1-MCP, and 1-butene.

Experiment 1 evaluated ethylene adsorption and desorption capabilities of MOFs and zeolite adsorbents and the impact CO₂ and water vapor on adsorption. Experiment 2 evaluated the adsorption and desorption of 1-butene. Experiment 3 evaluated 1-MCP adsorption and desorption. Experiment 4 was a proof-of-concept study to validate the utility of ethylene desorption from a MOF for ripening fruit using banana as a model plant material.

2.1. Materials

The MOFs, Basolite A520 (Al(III)/fumaric acid) and Basolite C300 (Cu(II)/benzene-1,3,5-tricarboxylate) and zeolite Z13X were obtained from Sigma-Aldrich Corporation (MO, USA). They were selected based on their high surface area (Table 1; information provided by BASF Corporation, Germany) and high sorption characteristics (Yilmaz et al., 2012). High purity ethylene and 1-butene gases were used (Matheson Gas Products, NJ, USA). High purity, compressed N₂ and CO₂ gas cylinders were from Airgas (MI, USA). 1-MCP was generated by release from SmartFresh™ (AgroFresh, Dow Chemical Company, PA, USA). A stock gas of 1-MCP concentration of approximately 15,000 μL L⁻¹, was created by dissolving 781.3 mg of SmartFresh™ powder in 10 mL of water inside sealed 480-mL glass jars as described in Vallejo and Beaudry (2006). These concentrations were determined relative to a 10 μL L⁻¹ 1-butene standard as described by Nanthachai et al. (2007). KNO₃ was obtained from Sigma-Aldrich Corporation (MO, USA).

Prior to use, Basolite C300 and A520 and zeolite Z13X were activated by subjecting them to high temperature (140 °C and 110 °C, respectively) and low pressure (27 Pa) for a minimum of 8 h in an oven (Despatch Industries, MN, USA). The vacuum was established in a 10-L glass desiccator using a vacuum pump.

In all experiments, 480-mL glass jars (Ball Corporation, CO, USA) were used to expose the adsorbents to gases of interest. The lids of the jars were fitted with half-hole, bilayer silicon/PTFE septa to permit gas sampling. Activated adsorbents were weighed using an analytical balance (XS105 Dual Range, Mettler-Toledo, Inc. OH, USA). After weighing, adsorbents were quickly placed inside the jars to avoid water adsorption from the environment, and the jars closed before or after the addition of the gases to be studied. Temperatures were controlled by placing the containers in temperature-controlled rooms that maintained temperatures ± 0.5 °C of the target temperature.

Table 1
Properties of the three adsorbents characterized in this study.

Material/Adsorbents	Metal constituents	Organic linker	Pore diameter [Å]	Particle size (μm)	Langmuir surface area (m ² /g)	Hydrophilicity
Basolite C300	Cu	Trimesic acid	3.5 and 9	20–100	2000	hydrophilic
Basolite A520	Al	Fumaric acid	11.5	20–100	1300	hydrophilic
Zeolite Z13X	Si, Al	n.a.	8	1–4	570	hydrophilic

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