Factors Affecting Ethylene Adsorption by Zeolite: The Last Word (from us)

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Introduction

Many vegetables, fruits and flowers are sensitive to ethylene and early senescence can occur when these commodities are exposed to low concentrations (near 1 µL L^{-1}) of ethylene. During transport or storage certain commodities can produce ethylene that can lead to a reduction in their quality and shelf-life or to that of other ethylene-sensitive commodities transported or stored along with the ethylene-producing commodity. In addition, damaging concentrations of ethylene are often present at shipping points or distribution centers due to poorly vented ripening/conditioning rooms, propane lift trucks, and other environmental sources. One of the most effective materials to remove ethylene is potassium permanganate and commercial products are available using it. However, due to the chemical properties of potassium permanganate, precautions must taken to prevent contamination of food products. Waste disposal may be an additional issue. The search for other materials with ethylene removal capability and with fewer precautions has focused much attention on zeolite.

Zeolites are aluminosilicate minerals having a three-dimensional framework structure with interconnected cages and channels. There are about 40 natural zeolites and a large number of synthetic zeolites with various properties including cation exchange, adsorption, molecular sieving, dehydration and rehydration. These properties enable zeolites to have many industrial and agricultural applications including water and gas purification, hazardous waste cleanup, and as amendments to animal feeds and soils. Zeolite adsorption of ethylene and other gases for use in the purification of natural gas has been well characterized. Since zeolites and zeolite-impregnated films or paper carton-liners are being marketed for ethylene adsorption with horticultural commodities we examined two commonly used, natural zeolites for their ability to adsorb ethylene (reported in PHQ 92 Nov. 1997) and, in this brief report, the influence of relative humidity upon ethylene adsorption.

Summary Conclusions

The Chabazite zeolite adsorbed ethylene if it was heat-treated, 150ºC for 15 h and 25 inches of mercury vacuum, before the test, while the Clinoptiloite zeolite did not adsorb ethylene, with or without heat treatment. When 1.0 g of Chabazite with adsorbed ethylene, 3.3 µL, was subsequently exposed to near 100% relative humidity (RH), more than 95% of the ethylene was displaced after 3 h. Heat-treated Chabazite placed in near 100% RH for 1.5 h before ethylene application lost essentially all ethylene adsorption ability. When 1.0 g of heat-treated Chabazite with adsorbed ethylene, 3.3 µL, was exposed to 48% relative humidity, about 90% of the ethylene was displaced (fig. 1).

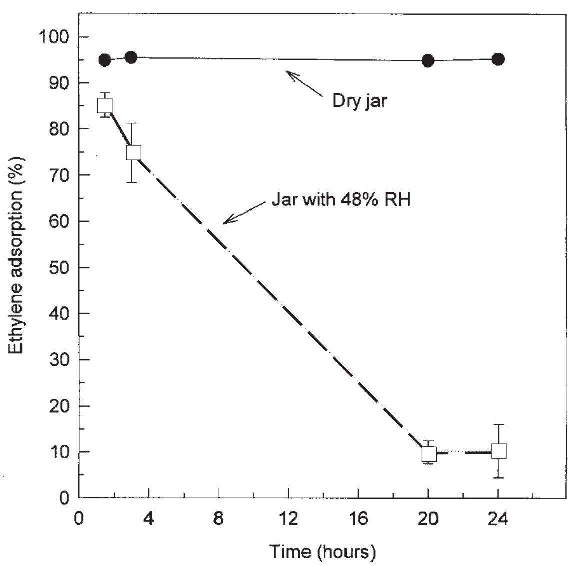

Figure 1. *After 1.5h exposure to a controlled 48% RH environment, heated zeolite lost 10% of its C_2H_4 adsorbing capacity. After 20 h exposure, only 10% of this capacity was retained.*

In contrast, the *Ethylene Control* packet (a potassium permanganate-based product) removed all of the applied ethylene within 1 h and had an ethylene removal capability of about 6,500 µL/7 g packet.

Flowers and vegetables are generally stored/ transported in high humidity conditions; usually 80% relative humidity or higher. For an ethylene removal product to be useful, it therefore must be effective under high humidity conditions. At this time, the effectiveness of current zeolite-based products used for ethylene removal from horticultural commodities is probably very limited. Yet, in this study we only examined two of the reported 40 natural zeolites. Possibly some of the other natural or synthetic zeolites have adsorption affinities for ethylene that are much greater than that for water vapor enabling them to have a practical application for ethylene removal with horticultural commodities.

Additional Results and Discussion

Since only the heated Chabazite zeolite exhibited the ability to remove ethylene (Fig. 2), we examined this zeolite further.

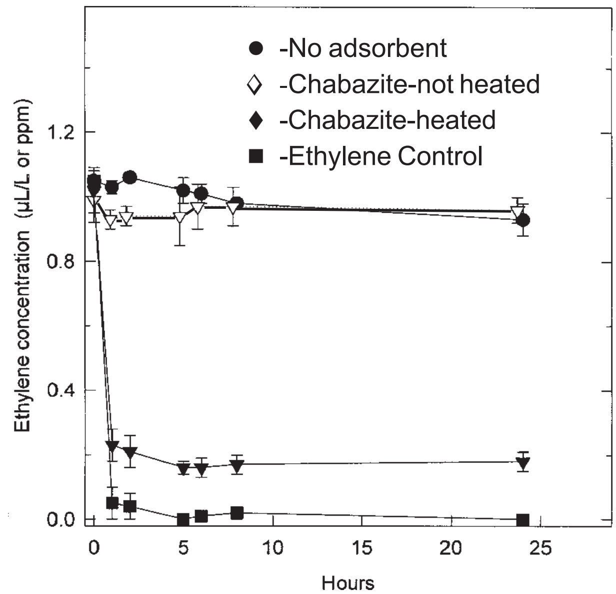

Figure 2. *Chabazite-type zeolite, heated to 150ºC for 15h, adsorbs up to 94% of the added C_2H_4 in the test system.*

When the zeolite was heated (150ºC for 15 h with vacuum of 25 inches of mercury) and tested immediately, it adsorbed about 94% of the ethylene added (Fig. 3). In this experiment, 1.0 g of zeolite was tested with a range of ethylene concentrations from 0.13 to 7.4 µL L^{-1}. Results strongly suggest that other volatiles or water vapor can occupy some or all of the ethylene adsorption sites unless these other volatiles are removed by heating. The results also indicate that a constant proportion of ethylene, over the concentration range tested, is adsorbed; the ethylene partitions between the air and Chabazite.

Materials and Methods Overview

Ethylene removal was measured by placing each product in a 1 quart jar (0.946 L), then sealing with a gasket and screw-cap lid. Ethylene was injected into

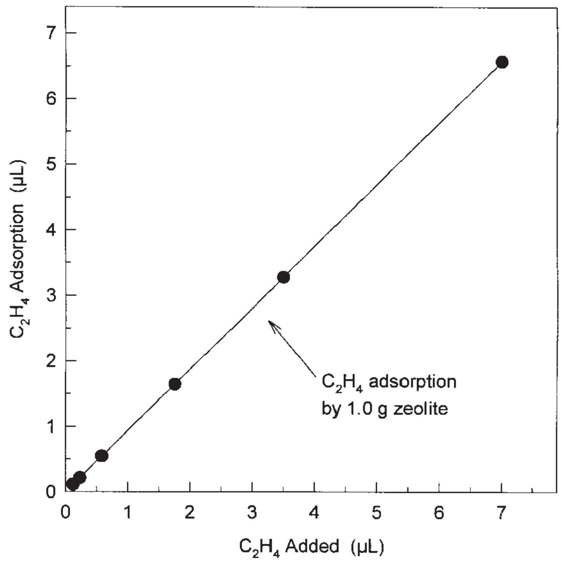

Figure 3. *Heated zeolite adsorbs C_2H_4 over the range of concentrations commonly found in commericial storage and distribution environments. For each concentration, 94% of the C_2H_4 was adsorbed.*

the jar to give a specific concentration, usually from 1 to 7 µL L^{-1} (ppm). The jars were held at 68ºF (25ºC) with ambient relative humidity (30 to 40%) and ethylene concentration in the jars was measured periodically using a gas chromatograph with an alumina/5% NaCl column at 80ºC and flame ionization detector. The following amounts of each product were individually tested in each jar: 1.0 or 3.0 g of zeolite particles and 1 packet of *Ethylene Control* containing about 7 g of potassium permanganate formulated material. Ethylene adsorption was calculated by taking the difference between the amount of ethylene added and the amount remaining in the headspace. Triplicate samples of each product were tested. Replicated, sealed ethylene-containing jars without product were included in most experiments as a control.

After preliminary experiments indicated that the zeolite particles must be heated before ethylene adsorption would occur, the particles were routinely heated at 150ºC for 15 h under a vacuum of 25 inches of mercury immediately before each experiment, unless otherwise specified. The particles were allowed to cool 5 to 10 minutes before they were placed in the quart jars.

The ethylene adsorption capacity of the zeolite particles was examined using a range of ethylene concentrations from 0.13 to 7.4 µL L^{-1} in the 1 quart jars with 1.0 g of zeolite particles. The ethylene removal capacity of the *Ethylene Control* product was determined by continuing to add ethylene over a 24 h period to a quart jar containing 0.5 g of the product until no further ethylene was removed.

The influence of near 100% relative humidity on ethylene removal by the zeolite particles was examined by placing the particles in plastic Petri dishes inside quart jars lined with water-saturated filter paper. Ethylene adsorption was measured before and after transfer to the humid jar. The influence of 48% relative humidity on ethylene adsorption was examined using a saturated solution of potassium nitrite to generate this humidity level at 15ºC.

Background Literature

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A full report of this project is being submitted to an international horticultural science journal and will be available for release following peer review.