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Effect of Doping Natural Zeolite with Copper and Zinc Cations on Ethylene Removal and Postharvest Tomato Fruit Quality

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Tomatoes (*Solanum lycopersicum* L.), one of the most consumed vegetables worldwide, are climacteric fruit in which ripening is accompanied by quickly increased respiration and ethylene production. Ethylene stimulates ripening and senescence that finally may result in detrimental effects by promoting unwanted softening, grainy structure, accelerated pigment synthesis and chlorophyll loss in tomatoes. Therefore, most postharvest technology strategies are focused on the minimization of ethylene production, inhibition of its action and removal of ethylene from storage facilities. The aim of the present work was to study the ethylene adsorption capacity of a novel copper-zinc-based ethylene scavenger supported on natural zeolite and the effects of ethylene scavenging on quality attributes of tomatoes during their postharvest shelf life. Tomatoes (control, natural zeolite, zeolite doped with copper and zinc) were stored in hermetically sealed glass desiccators, in darkness at 20 °C and a relative humidity of 88 %. Production rates of ethylene and carbon dioxide were determined during 15 days of storage of tomato fruit by monitoring their headspace concentrations as a function of time using gas chromatography. Physical parameters, such as size, weight, colour and texture, and chemical attributes, including moisture, soluble solids, titratable acidity, reducing sugars and lycopene, were determined at the start of the experiment and after 8 and 15 days of tomato storage. Ethylene production diminished in 50 % for modified zeolite and in 7 % for natural zeolite during the first week, while major concentration peaks appeared for both zeolite treatments at 9.5 days. Moreover, modified zeolite delayed tomato respiration during the first six days. This adsorbent was able to shift the respiration peak compared to control treatment in time due to the incorporation of copper and zinc. Increased respiration and ethylene production rates in presence of both zeolites after 1 week of tomato storage trigger the decay of organic acids and part of the soluble solids. In addition, natural zeolite significantly reduced Young's modulus at the end of storage, which can be attributed to the increased ethylene accumulation of about 40 % compared to control tomatoes. Furthermore, red colour evolution was promoted by natural zeolite, while modified zeolite induced the greatest delay of colour development in tomatoes. Additionally, the use of natural zeolite results to significantly higher increase of lycopene synthesis compared to tomatoes stored in presence of modified zeolite. Natural zeolite doped with copper and zinc cations favours ethylene removal and delays tomato fruit ripening. However, the single use of natural zeolite should be reconsidered due to its ripening promoting effects in tomatoes. Finally, the incorporation of copper and zinc cations to a zeolite support is a new, emergent postharvest technology to slow down fruit ripening that may create new commercial opportunities for fresh-market tomatoes.

1. Introduction

Ethylene (C₂H₄), a relatively simple hydrocarbon molecule that consists of two carbon atoms linked by a double bond, controls and regulates a large number of physiological processes from seed germination to organ senescence in fruit and vegetables. From a postharvest point of view, ethylene confers a double, but

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reverse effect. First, it stimulates ripening of climacteric fruits such as tomatoes, resulting in desirable changes in flavour, colour and textural characteristics. On the other hand, acceleration of ripening by ethylene results in a reduced postharvest life (Martínez-Romero et al., 2007). Therefore, a suitable control of the ethylene concentration and action by the removal of excess of ethylene from storage facilities helps to avoid the detrimental effects of this plant hormone on fruit quality and prolongs their storability.

Several low cost materials have been investigated for their potential application as adsorbents for ethylene. Among these materials, natural zeolites are one of the most promising materials for ethylene removal. Zeolites are crystalline aluminosilicates of alkali and alkaline earth elements composed of a tetrahedral framework of SiO_4 and AlO_4 (Erdoğan et al., 2008). Due to their large surface area and cation exchange capacity, zeolites act as molecular sieves in purification processes (Erdoğan et al., 2008). Other properties such as their non-toxicity, abundance, economic and environmental acceptability, make zeolites as outstanding sorbent materials for the agro-food industry (Wibowo et al., 2017). Upon the substitution of silicon by aluminium atoms in the zeolite framework, the surface becomes negatively charged and additional metal cations or hydroxyl protons should be introduced to balance charge, forming weak Lewis acid or strong Brønsted acid sites, respectively (Almulla et al., 2017; Abreu et al., 2019). The ability to exchange divalent transition metals as compensating cations improves the adsorption and catalytic properties of zeolites. In particular, the ionic radius of divalent cations is less than of monovalent cations and may improve the access of ethylene to the adsorption sites. Zeolites with divalent counter cations such as Cu^{2+} and Zn^{2+} show preferential ethylene adsorption due to the interaction between the double charged cations and the quadrupole moment of ethylene (cation- π interaction) (Patdhanagul et al., 2010). Former interaction is additional to weak H-bonding interaction between highly electronegative oxygen present on the natural zeolite surface with the hydrogen of the C-H bond of ethylene (Sue-aok et al., 2010).

The aim of the present work was to study the ethylene adsorption capacity of a novel copper-zinc-based ethylene scavenger supported on natural zeolite and the effects of ethylene scavenging on quality attributes of tomatoes during their postharvest shelf life.

2. Experimental

2.1 Zeolite preparation

Natural zeolite (Minera Formas, Parral, Chile) ground and sieved to an average particle size of $360\pm60\ \mu\text{m}$, was rinsed, filtered and dried ($105\ ^\circ\text{C}$, 24 h). Cation exchange of zeolite samples (0.10 w/v) was done using 0.1 M ammonium sulphate by stirring at 27 rpm ($90\ ^\circ\text{C}$, 2 h), followed by a washing step with deionised water for 4 h. After repeating these ion exchange and washing procedures once again, zeolite samples were thermally degassed ($350\ ^\circ\text{C}$, 2 h) in presence of argon. Pre-treated samples (0.10 w/v) were modified by metal ion exchange using both copper and zinc nitrate (66.4 mM) ($90\ ^\circ\text{C}$, 24 h) under stirring (27 rpm). After repeating the rinsing, drying and degasification procedures, modified zeolite doped with copper and zinc cations was activated by heating at $350\ ^\circ\text{C}$ for 4 h under an oxygen atmosphere (Abreu et al., 2019).

2.2 Postharvest treatments

Tomato fruit (*Solanum lycopersicum*, cv. Medano), harvested at breaker stage, were separated into three groups (natural zeolite (Z), modified zeolite (Z – Cu/Zn) and control) and each group consisted of three lots. Tomatoes ($\pm750\ \text{g}$) were stored in hermetically sealed glass desiccators (10 L) at $20\ ^\circ\text{C}$ in darkness and 88% relative humidity (RH) with 10 g natural zeolite, 10 g modified zeolite or in absence of zeolite, respectively. Ethylene and carbon dioxide production rates were determined during 15 days by analysing the headspace atmosphere composition of each desiccator as a function of time using gas chromatography. Physical parameters, such as size, weight, colour and texture, and chemical attributes including moisture, soluble solids, titratable acidity, reducing sugars and lycopene content were determined at the start and after 8 and 15 days of tomato storage. Details about experimental conditions have been described elsewhere (Gómez, 2018).

3. Results and discussion

3.1 Ethylene and carbon dioxide production

Ethylene production of control showed a main peak during the first week of tomato storage, while zeolite treatments, in particular copper and zinc modified zeolite, promote major ethylene formation during the second week of tomato storage (Figure 1). Ethylene production diminished in 7% for natural zeolite and in 50% for modified zeolite during the first week. Zeolite capacity increased by ion exchange with copper and zinc,

promoting ethylene removal from high moisture and oxygen environments. Carbon dioxide production showed a similar behaviour with a strong increase for zeolites during the second week of storage (Figure 2).

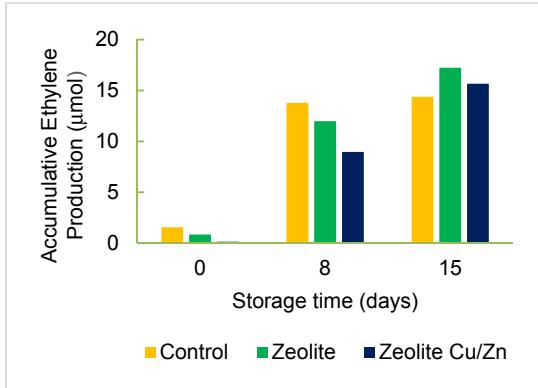


Figure 1: Accumulative production of ethylene as a function of storage time for different treatments.

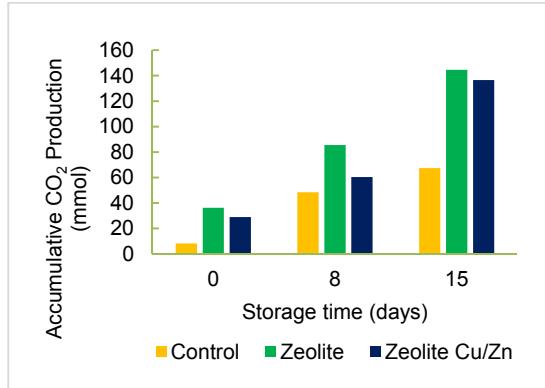


Figure 2: Accumulative production of carbon dioxide as a function of storage time for different treatments.

Initial CO_2 formation in presence of zeolites may be due to the CO_2 desorption from zeolites into the headspace driven by water vapour. Ethylene scrubbing by adsorbents lowers the ethylene concentration in the gaseous headspace, promoting gradient formation of ethylene and therefore its diffusion across tomato skin and flesh barriers while diminishing internal ethylene concentration. However, autocatalytic ethylene synthesis may finally result in a sharp increase of internal ethylene concentrations (>100 ppm) (Saltveit, 1999), yielding an unsteady state between the accelerated ethylene production rate and mass transfer limited adsorption rate. The composition of the gas mixture affects the adsorption capacity and predominant surface speciation for zeolites. In particular, high moisture and oxygen conditions diminished the adsorption capacity of zeolite, while the greatest removal of C_2H_4 occurs in presence of nitrogen (Smith et al., 2009). In the absence of water and oxygen, the conversion of ethylene to ethylidyne species enables the interaction *via* triple carbon bonds to surface metal atoms. Contrary, the presence of oxygen favored π -bonded ethylene over σ -bonded ethylene adsorption (Smith et al., 2009). It has been suggested that ethylene adsorption is mainly governed by weak hydrogen bonding interactions among CH atoms of ethylene and O atoms of terminal Si-OH and Si-OH-Al bridges in the case of natural zeolites (Patdhanagul et al., 2010; Abreu et al., 2019). However, the incorporation of Cu^{2+} and Zn^{2+} ions after ion exchange treatments into the zeolite structure decreased the contents of monovalent compensating cations, while increasing microporous surface area and microporous volume (Abreu et al., 2019). Additional ion-induced dipole interactions between the ethylene molecules and the new compensating cations located on the zeolite surface improve ethylene binding *via* the interaction among π -electrons of ethylene and orbitals of compensating cations within the zeolite framework (Sue-aok et al., 2010). Copper exchanged zeolite showed the greatest adsorption capacity for ethylene, although this material is more sensitive to moisture (Abreu et al., 2019). The incorporation of zinc makes zeolite less susceptible to high moisture conditions. In the presence of moisture, water and ethylene molecules compete for the active adsorption sites of zeolites (Abreu et al., 2019) as the CH-O interactions for ethylene are weaker than the OH-O interactions between water and zeolite (Sue-aok et al., 2010), blocking the ethylene interactions with zeolite and diminishing considerably the ethylene adsorption at the final stage.

Despite of ethylene scavenging of zeolites during the first week of tomato storage, respiration rate did not decrease during the first week according to CO_2 accumulation data (Figure 2). However, these results were influenced by the high initial respiration rate because of the accommodation of tomatoes and adsorbents, promoting CO_2 desorption in desiccator headspace. Our zeolites are considered as hydrophilic (atomic ratio of silica and alumina is roughly five) with a water adsorption capacity higher than the one for CO_2 (Hefti et al., 2014). Modified zeolite was able to shift the respiration peak for 7 days compared to control. This resulted in CO_2 concentrations of about 9 %, being out of the recommended range of 2-5 % for tomatoes. These high levels of CO_2 may reduce the sensitivity to ethylene and inhibit ethylene action in tomatoes (Saltveit, 2003).

3.2 Effects of zeolites on tomato quality

Excessive loss of moisture in fresh fruit yields a considerable weight reduction, being generally associated with loss of freshness. In this study, no significant effect of adsorbents on weight loss of postharvest tomatoes was found (Figure 3). Moreover, titratable acidity is another essential quality parameter for tomatoes that decreased during ripening (Figure 4). Zeolites promote a slightly better retention of organic acids during the

first week of tomato storage, while increased respiration and ethylene production after 1 week for stored tomatoes in presence of both zeolites may trigger the decay of organic acids, such as citrate and isocitrate that are part of the soluble solids (Figure 5). The stronger decay of soluble solids for zeolite samples compared to control treatment during the second half of storage seems to be related to the loss of organic acids due to the increased respiration of stored tomatoes. About 45% of the total solids in tomato fruit is composed of soluble solids, predominantly reducing sugars. Zeolites did not alter the evolution of reducing sugars over time (Figure 6).

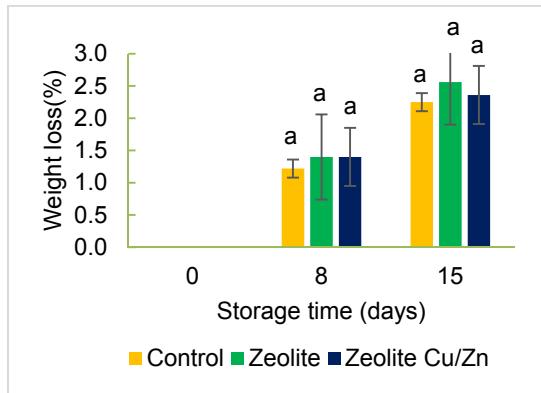


Figure 3: Weight loss of tomatoes as a function of storage time for different treatments. Bars indicate standard error for mean values. Different letters for the same day mean significant difference at $P \leq 0.05$.

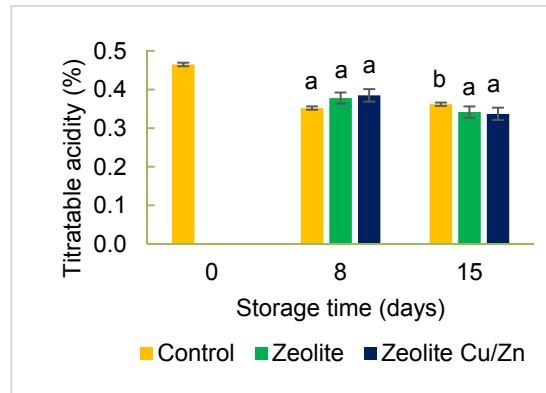


Figure 4: Titratable acidity of tomatoes as a function of storage time for different treatments. Bars indicate standard error for mean values. Different letters for the same day mean significant difference at $P \leq 0.05$.

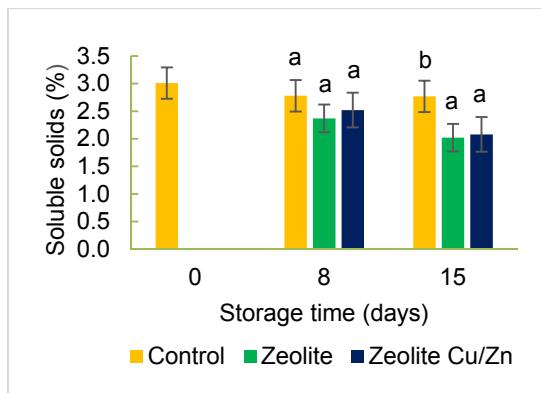


Figure 5: Soluble solids in tomatoes as a function of storage time for different treatments. Bars indicate standard error for mean values. Different letters for the same day mean significant difference at $P \leq 0.05$.

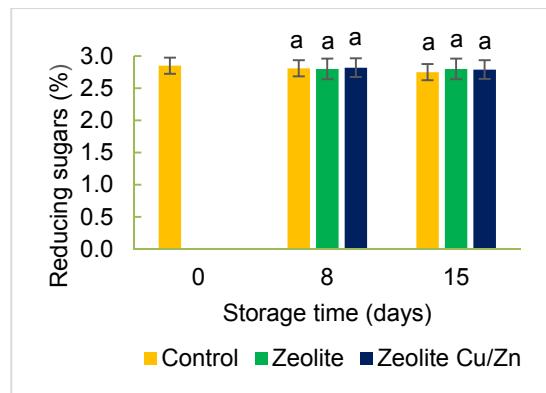


Figure 6: Reducing sugars in tomatoes as a function of storage time for different treatments. Bars indicate standard error for mean values. Different letters for the same day mean significant difference at $P \leq 0.05$.

Fresh-market tomatoes, commonly harvested at mature green or breaker stage become soft as ripening proceeds during storage. For this kind of tomatoes, texture is one of the most important quality attributes, influenced by both skin strength and flesh firmness. Skin strength depends on the initial force at the bioyield point, required to punch through the pericarp of tomatoes. Skin strength drops quickly during the first stage of storage followed by a more gradual decrease without any significant difference between treatments (Figure 7). Flesh firmness or mesocarp strength can be calculated from the Young's modulus. Natural zeolite significantly reduced the Young's modulus at the end of storage (Figure 8), which could be attributed to increased ethylene accumulation of about 40% compared to control tomatoes. Softening of fruit flesh is mainly attributed to the degradation of pectins catalysed by cell wall degrading enzymes, induced by ethylene, which may result in a reduced integrity of cell wall components, loss of membrane integrity and cell turgor. This, in turn, affects shelf life and consumer's acceptance of tomatoes. Colour is the most important external attribute to assess tomato ripeness and shelf life being the major factor for consumer's purchase decision. In this study, ripening is accompanied by a loss of initial green orange colour associated to the breaker stage and the development

of pink (after 1 week) and light red colour characteristics (after 2 weeks) for modified zeolite and control tomatoes. Moreover, tomatoes treated with natural zeolite evolved an accelerated colour change expressed by the development of light red (after 1 week) and red colour characteristics (after 2 weeks) according to USDA colour standards. In addition, the greatest effect on delaying colour development in tomatoes was found for zeolite that incorporates copper and zinc cations (Figure 9). Red colour development is the result of chlorophyll degradation, as well as the synthesis of carotenoids, as chloroplasts are converted into chromoplasts. Hue angle h^* correlates well with consumer's perception of fruit colour. A hue angle greater than 90° in the second quadrant of the $L^* a^* b^*$ colour space represents the initial condition of raw material and indicates a green orange colour of tomato surface (Figure 9). During ripening, hue decreased rapidly up to 47° for zeolite treated tomatoes corresponding to a light red colour, while hue of the other tomato samples was in the $70\text{--}72^\circ$ range after 8 days of storage, which corresponds to a pink colour (Figure 9). Natural zeolite promotes red colour evolution of tomatoes, which coincides with an increase of 100% in the amount for CO_2 produced after 8 days of storage in comparison to control. The inclusion of copper and zinc cations within the zeolite matrix is favourable, avoiding an excessive red colour development of tomatoes treated by natural zeolite. Positive health benefits were associated to the consumption of a diet rich in lycopene, a fat-soluble carotenoid with excellent antioxidant properties. The accumulation of lycopene occurs due to the conversion of chloroplasts into chromoplasts, coupled to the synthesis of this red pigment. Lycopene content of tomatoes correlated positively to both surface and puree colours. This suggests that lycopene content depends upon tomato ripeness. Our results indicate that lycopene content of tomatoes increased progressively over time ranging between 9.2 and 62.5 mg kg^{-1} (Figure 10).

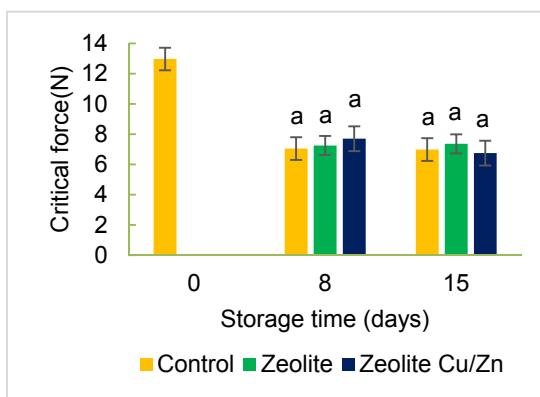


Figure 7: Critical force in bioyield point of tomatoes as a function of storage time for different treatments. Bars indicate standard error for mean values. Different letters for the same day mean significant difference at $P \leq 0.05$.

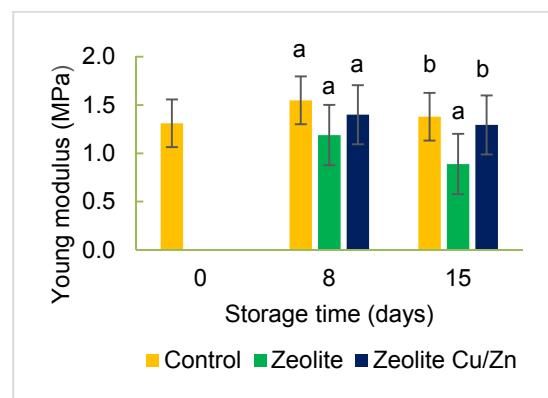


Figure 8: Young's modulus of tomatoes as a function of storage time for different treatments. Bars indicate standard error for mean values. Different letters for the same day mean significant difference at $P \leq 0.05$.

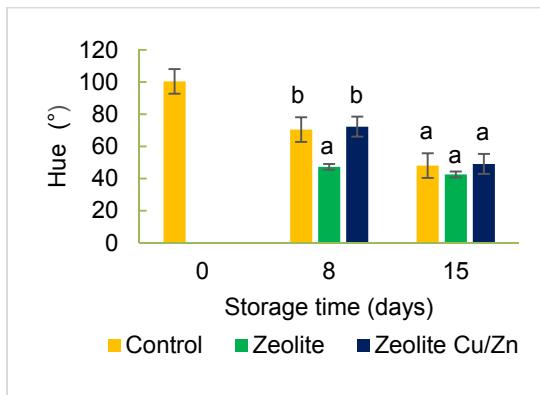


Figure 9: Hue of tomatoes as a function of storage time for different treatments. Bars indicate standard error for mean values. Different letters for the same day mean significant difference at $P \leq 0.05$.

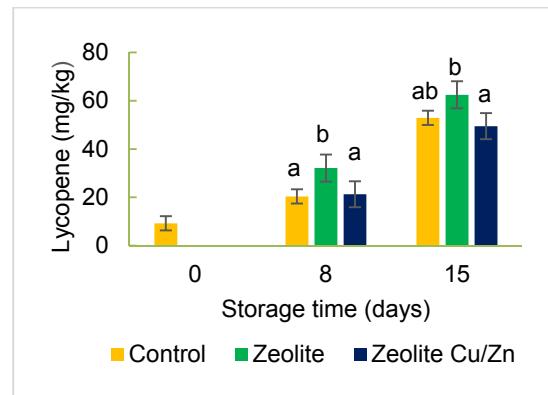


Figure 10: Lycopene content of tomatoes as a function of storage time for different treatments. Bars indicate standard error for mean values. Different letters for the same day mean significant difference at $P \leq 0.05$.

Moreover, lycopene content had a strong negative correlation with hue while lycopene synthesis was also affected by ethylene and CO₂ levels inside the gas atmosphere of the desiccator. In addition, natural zeolite yields significantly higher increase of lycopene synthesis compared to tomatoes stored in presence of modified zeolite (Figure 10). Finally, improved ripening of tomatoes in presence of natural zeolite is negative if our aim is to increase postharvest shelf life, while the incorporation of copper and zinc cations to the matrix support slows down fruit ripening being an emergent postharvest technology that may create new commercial opportunities.

4. Conclusions

This study assessed the use of natural and modified zeolites for ethylene removal from tomato storage systems. Natural zeolite induced tomato ripening according to titratable acidity, soluble solids, Young's modulus and hue after fifteen days of tomato storage. Zeolite doped with copper and zinc cations was able to remove 50% of produced ethylene after the first week of storage and to shift the respiration peak for seven days compared to control. Hue and lycopene improved after eight days and Young's modulus and lycopene after fifteen days of storage. Doping of zeolite with copper and zinc cations seems to favour ethylene adsorption by cation-π interactions, improving postharvest tomato quality. Higher concentrations of copper and zinc could increase the efficiency of ethylene removal. Finally, the use of ultraviolet light should be explored to degrade bound ethylene and make free the active sorption sites of modified zeolite.

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