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# Efficient ethylene removal of silver-exchanged zeolite X for fruit preservation

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#### ABSTRACT

Ethylene accelerates fruit ripening, leading to significant postharvest losses. This study synthesized silver-exchanged zeolite X (Ag/ZX) via vacuum-assisted ion exchange and evaluated its ethylene removal efficiency and banana preservation performance. Material characterization confirmed preserved zeolite X structure (XRD) with uniform Ag dispersion (EDX mapping, 2.49 wt% Ag loading). The optimal 0.7 mmol Ag/ZX sample demonstrated 90% ethylene removal (0.2 g material, 1000 ppmv C<sub>2</sub>H<sub>4</sub>, 30 °C) within 180 min, outperforming pure zeolite X (11%) and lower-Ag samples (30% for 0.1–0.3 mmol Ag/ZX). Notably, Ag/ZX exhibited dual adsorption-oxidation functionality, with 0.1 mmol/g ethylene uptake capacity at 0.056 mmol/L initial concentration. The material maintained > 82% efficiency after two regeneration cycles (400 °C treatment). In banana storage trials, Ag/ZX delayed ripening by 4 days versus controls, reducing natural weight loss to < 5% after 6 days (vs. 12% in controls) and inhibiting mold growth. The results highlight Ag/ZX as a cost-effective, regenerative solution for ethylene control, with direct applications in tropical fruit preservation.

Keywords: ethylene removal, zeolite X, silver nanoparticles, adsorption-oxidation, postharvest losses.

### INTRODUCTION

Vietnam, endowed with a monsoon tropical climate and remarkable geographical diversity, possesses substantial potential for fruit and vegetable production and export. However, this sector faces significant challenges, evidenced by declining export values and high postharvest loss rates estimated at 20-30%, resulting in annual economic losses reaching billions of US dollars (Le, 2022; Truong, 2018). A primary contributing factor is the limitation in preservation and processing technologies, particularly in controlling ethylene - a natural plant hormone that accelerates fruit ripening and consequently reduces shelf life. At the beginning of ripening, climacteric fruits experience a sudden increase in respiration and a rapid rise in ethylene production. Ethylene acts as an important signal to begin and regulate

the ripening process. Even if the ethylene concentration is as low as one ppm, ethylene affects the quality of most agricultural goods (Chauhan et al., 2025). Understanding how an excess amount of ethylene can ruin the fruit's storage, it is important to control its level to keep fruits fresh for longer. This helps reduce losses after harvest (Bianchetti et al., 2024).

Common methods for removing ethylene include ventilation, biodegradation, direct oxidation, catalytic oxidation, and adsorption. While ventilation is widely used, it has high energy costs and is less effective for trace amounts of ethylene. Biodegradation is effective but requires long processing times and strict operating conditions. Oxidation methods generally require high temperatures and may produce secondary pollution (Qi et al., 2024). In particular, exogenous ethylene scavenging agents such as potassium permanganate (KMnO<sub>4</sub>) chemical oxidation (Ferreira et al., 2024) and ozone (O<sub>3</sub>) advanced oxidation systems (Ferreira et al., 2024) can be used for oxidizing ethylene into carbon dioxide, however it also has some disadvantages according to Haiying Wei et al's study (Wei et al., 2021). Another specific application is using photocatalytic technology. The use of photocatalytic technology to degrade ethylene has the advantages of simplicity, mild reaction conditions and fast reaction rate (Cheng et al., 2024). In catalysis field, a BMT-based hydrogel film by incorporating the electrospun necklace-like BMT photocatalyst into a polyvinyl alcohol (PVA) and glycerol hydrogel was developed. This innovative material excels in ethylene removal, while also possessing excellent self-healing and antibacterial properties (Lu et al., 2025). However, this material utilizes sunlight to convert ethylene into CO2 and H<sub>2</sub>O. Therefore, in the absence of light – such as during long-term fruit transportation in sealed packaging - this method may be less effective. Adsorption can overcome this difficulty, since it can happen in normal conditions. However, commonly used ethylene removal materials, such as activated carbon and zeolite, exhibit weak affinities for ethylene, which hinders their effectiveness in adsorbing ethylene under ambient pressure (Jiang et al., 2025). As a consequence, it is necessary to find a way to modify adsorbent to enhance its efficiency. Among them, a promising method is doping a suitable metal onto the adsorbent surface to enhance ethylene adsorption performance.

Studies have confirmed that Ag<sup>+</sup> plays a key role in ethylene adsorption through  $\pi$  interaction (Ferreira et al., 2024). AgNPs can be applied for fruit and vegetable preservation by immersing or incorporating AgNPs into wrapper film or edible coating (Lieu et al., 2024). For wrapper film, this action can enhance anti-microorganism ability. Nevertheless, since film are usually made of organic materials such as chitosan, sodium alginate, etc. are unable to withstand high temperature. Therefore, it is difficult for regeneration material to reuse the material if this step needs extreme temperature conditions. In contrast, zeolites are commercially available and easily regenerable (Ferreira et al., 2024). Thus, metals inside zeolites pores can be beneficial since they readily interact with ethylene, by the so-called  $\pi$  interaction, Ag-based zeolite materials have been extensively studied.

Recent studies have demonstrated Ag/zeolite's exceptional ethylene removal capacity through dual adsorption-oxidation mechanisms at ambient temperatures (Cisneros et al., 2019; Ferreira et al., 2024; Qi et al., 2021; Yang et al., 2018). Nevertheless, significant challenges remain, including the need to optimize Ag/zeolite materials for enhanced efficiency, cost reduction, and simplified synthesis protocols. Notably, research on ethylene removal using silvermodified zeolite X (Ag/ZX) remains limited, while previous studies have predominantly focused on other zeolite types (ZSM-5, 5A, Mordenite, Beta, and Y).

This study specifically investigates the synthesis and ethylene removal performance of Ag/ZX materials, with dual objectives: (1) maximizing ethylene elimination efficiency and (2) extending the shelf life of tropical fruits, particularly bananas. The research aims to contribute to both materials innovation and the economic viability of postharvest preservation technologies in Vietnam's agricultural sector.

### MATERIAL AND METHODS

### Syntheses and characterization of Ag/Zeolite X

Zeolite X used in this study was synthesized by the traditional hydrothermal method according to the procedure published in the reference document (Robson, 2001). Silver nitrate (AgNO<sub>3</sub>,  $\geq$  99.8%) was procured from Changzhou Guoyu Co., Ltd. (China). All Ag/ZX materials were synthesized via vacuum-assisted ion exchange, a method selected to enhance silver dispersion efficiency within the zeolite X matrix. Figure 1 illustrates the vacuum-assisted ion exchange protocol for synthesizing silverexchanged zeolite X (Ag/ZX). In a typical procedure, 3.0 g of zeolite X was mixed with x mL of 0.15 M AgNO3 solution under vacuum conditions for 2 h, followed by continuous stirring at room temperature in dark conditions for 12 h. The ion-exchanged product was then filtered, thoroughly washed with deionized water, and dried at 80 °C for 8 h. Final calcination was performed at 600 °C for 2 h in static air to achieve optimal silver activation.

The physicochemical properties of the Ag/ ZX composites were systematically characterized using multiple analytical techniques. Crystal structure analysis was performed by X-ray diffraction (XRD; Rigaku SmartLab) using Cu K $\alpha$  radiation ( $\lambda = 1.5418$  Å) at 40 kV and



Figure 1. Ag/zeolite X synthesis procedure

30 mA, with a scanning range of  $5-50^{\circ}$  (2 $\theta$ ) at a rate of 0.02°/s. Surface area and porosity were evaluated through N2 adsorption-desorption isotherms (BET method; Micromeritics ASAP 2020). Morphological features and elemental distribution were examined by scanning electron microscopy (SEM; JEOL JSM-7800F Prime, Japan) coupled with energy-dispersive X-ray spectroscopy (EDX; Oxford Instruments). Surface functional groups were analyzed using Fourier-transform infrared spectroscopy (FTIR; Nicolet iS50, Thermo Scientific) in the range of 4000-400 cm<sup>-1</sup>. This comprehensive characterization approach ensured thorough evaluation of the structural, textural, and chemical properties of the synthesized materials.

### Ethylene removal performance evaluation

The ethylene removal performance of Ag/ ZX materials was evaluated using a sealed glass reactor system with a rubber septum. A known concentration of ethylene gas was injected into the reactor, and the adsorption process was monitored over time. Ethylene removal efficiency was quantified by gas chromatography (GC, HP 5980) equipped with a Varian CP-Sil 8 CB capillary column ( $30 \times 0.32 \text{ mm} \times 0.25 \text{ }\mu\text{m}$ ) and flame ionization detector (FID). The GC operating conditions were maintained at 150°C for the injector, 150 °C for the column, and 200°C for the FID detector, using highpurity nitrogen (99.99%) as the carrier gas. Gas samples (0.2 mL) were automatically injected every 60 minutes, with each data point representing the average of 3–5 replicate measurements to ensure accuracy. The experiment was repeated three times to ensure accuracy, then the average value and corresponding error were calculated.

The ethylene removal efficiency  $(\psi)$  was calculated using the formula:

$$\psi_i = (1 - \frac{A_i}{A_0}) \times 100 \tag{1}$$

where:  $A_0$  represents the initial peak area of ethylene (control measurement),  $A_i$  denotes the peak area at measurement interval *i* (typically every 60 minutes)

This normalized calculation method accounts for potential variations in initial ethylene concentrations across experimental runs. Peak areas were determined by integrating the signal from the FID detector at retention times corresponding to ethylene. Three to five technical replicates were averaged for each data point to ensure statistical reliability, with relative standard deviations maintained below 5% for all reported values.

### **RESULTS AND DISCUSSION**

### Characterization of Ag/zeolite X samples

As shown in Figure 2, the XRD patterns confirmed the high crystallinity of both pristine zeolite X and Ag-modified zeolite X (Ag/ZX). The Ag/ZX sample maintained all characteristic diffraction peaks of the FAU-type zeolite framework  $(2\theta = 6.2^{\circ}, 10.1^{\circ}, 11.9^{\circ}, 15.7^{\circ}, 20.4^{\circ}, 23.6^{\circ}, 27.1^{\circ},$ and  $31.4^{\circ}$ ), with no observable peak shifts or additional phases detected. Absence of new peaks at  $38.1^{\circ}$  (Ag<sup>0</sup>) or  $32.2^{\circ}$  (Ag<sub>2</sub>O) confirmed silver existed primarily as dispersed Ag<sup>+</sup> ions or nano-sized particles. These results collectively demonstrate that the silver species were uniformly incorporated into the zeolite framework while maintaining the structural integrity of the host material.

Scanning electron microscopy (SEM) analysis (Figure 3) demonstrated the morphological features of both pristine zeolite X and silvermodified Ag/ZX samples. The micrographs revealed well-defined octahedral crystals (1–2  $\mu$ m) characteristic of zeolite X, with no significant changes in particle size or shape after silver incorporation. However, higher magnification images showed noticeable surface smoothing in the Ag/ZX samples compared to the unmodified zeolite, suggesting uniform silver deposition within the pore structure rather than surface aggregation. Importantly, the preservation of crystal edges and facets confirmed that the ion exchange process did not damage the zeolite framework, consistent with XRD results (Thuan et al., 2024). The observed morphological stability indicates that the vacuum-assisted synthesis method successfully introduced silver species while maintaining the structural integrity of the host material - a critical factor for preserving the material's adsorption capacity and mass transfer properties. These findings correlate with the enhanced ethylene removal performance, as the intact crystal morphology ensures maintained porosity while the well-dispersed silver provides active sites. The uniform surface modification without particle aggregation further suggests optimal silver dispersion, which was subsequently confirmed by EDX elemental mapping analysis.

EDX is an analytical method that describes solid materials qualitatively and is frequently applied in conjunction with SEM (Hector et al., 2019). When electron beams interact with the target under examination, they produce distinctive X-ray lines corresponding to aspects of the sample (Scimeca et al., 2018). EDX mapping analysis (Figure 4) confirmed the presence and uniform distribution of silver throughout the Ag/ ZX composite, along with characteristic zeolite framework elements (O, Na, Al, Si). The homogeneous spatial distribution of Ag species, without any visible aggregation, demonstrates the effectiveness of the vacuum-assisted ion exchange method in achieving atomic-level dispersion of active silver sites. This optimal silver distribution



Figure 2. X-ray diffraction patterns of zeolite X and Ag/ZX synthesized sample



Figure 3. Scanning electron microscopy (SEM) photographs of (a,b) zeolite X and (c,d) Ag/ZX



Figure 4. EDX mapping of the Ag/ZX sample

creates abundant accessible active sites while maintaining open pore channels, which synergistically enhances both ethylene adsorption capacity and catalytic oxidation efficiency. The results provide direct evidence for the material's dual functionality in ethylene removal and potential VOC degradation, explaining its superior performance in fruit preservation applications. The uniform elemental distribution correlates well with the maintained crystallinity (XRD) and preserved morphology (SEM), completing the comprehensive characterization of this engineered adsorbent-catalyst material.

EDX quantitative analysis (Table 1) revealed significant changes in elemental composition following silver exchange. The sodium content decreased from 11.17% to 9.35% ( $\Delta 1.82\%$ ),

directly corresponding to the introduced silver content of 2.49 wt% (0.7 mmol Ag/g zeolite). This stoichiometric replacement confirms ion exchange predominantly occurred at sodium sites within the zeolite framework. Crucially, the silicon and aluminum contents remained constant (16.86%→16.16% Si, 11.46%→11.04% Al), with the Si/Al ratio virtually unchanged  $(1.47 \rightarrow 1.46)$ , demonstrating perfect preservation of the zeolite's aluminosilicate framework during modification. These results validate the selective nature of the exchange process and explain the maintained crystallinity observed in XRD patterns, as the fundamental building blocks of the zeolite structure remained intact while achieving precise silver loading control. The measured silver content (2.49%) matches the theoretical

Element	% Element		
Element	Before silver exchange	After silver exchange	
Oxygen	60.51 ± 0.22	60.95 ± 0.21	
Sodium	11.17 ± 0.10	9.35 ± 0.08	
Aluminum	11.46 ± 0.10	11.04 ± 0.08	
Silicon	16.86 ± 0.12	16.16 ± 0.11	
Silver	0	$2.49 \pm 0.04$	
Si/Al ratio	1.47	1.46	

**Table 1.** Elemental composition of zeolite X before and after ion exchange

exchange capacity of zeolite X for Ag<sup>+</sup> ions, confirming the efficiency of the vacuum-assisted synthesis method.

The 77 K N<sub>2</sub> adsorption-desorption isotherms (Figure 5) of Ag/ZX samples with varying silver loadings all exhibited characteristic Type I behavior according to IUPAC classification, confirming the preservation of microporous structure after silver modification. The isotherms showed a sharp nitrogen uptake at low relative pressures ( $P/P_0 < 0.01$ ) followed by a horizontal plateau, typical of microporous materials with uniform pore channels. While increasing silver loading from 0.1 to 0.9 mmol/g progressively reduced the N<sub>2</sub> uptake capacity by 5.9-16.8%, all samples maintained the essential Type I features including the sharp adsorption knee and minimal hysteresis, indicating the silver incorporation primarily occurred within the micropores without causing structural collapse or creating mesoporosity (Chen et al., 2022; Cisneros et al., 2019; Qi et al., 2021). These results demonstrate that the vacuum-assisted ion exchange method successfully introduced silver species while preserving the critical microporous framework necessary for efficient ethylene diffusion and adsorption, consistent with the XRD and SEM observations of maintained crystallinity and morphology. The systematic reduction in gas uptake quantitatively correlates with silver loading and provides direct evidence for the controlled deposition of active sites within the zeolite pore network.

Systematic analysis of the N<sub>2</sub> physisorption data (Table 2) revealed that silver incorporation progressively modified the textural properties of zeolite X while maintaining its fundamental microporous structure. Increasing the silver loading from 0 to 0.9 mmol/g resulted in a linear reduction of both surface area (S<sub>BET</sub>: 594.3  $\rightarrow$  494.6 m<sup>2</sup>/g, 16.8% decrease) and micropore volume (V<sub>micro</sub>: 0.2320  $\rightarrow$  0.1945 cm<sup>3</sup>/g, 16.2% decrease) between Ag content and parameter reduction. This proportional relationship indicates two concurrent mechanisms of silver deposition: (1) ion-exchanged Ag<sup>+</sup> cations occupying charge-balancing sites within the micropores, and (2) formation of small silver nanoparticles



Figure 5. N<sub>2</sub> adsorption-desorption curves of ZX and Ag/ZX samples

Sample	S <sub>BET</sub> (m²/g)	S <sub>micro*</sub> (m²/g)	S <sub>ext</sub> (m²/g)	V <sub>total</sub> (cm <sup>3</sup> /g)	V <sub>micro</sub> (cm³/g)
Zeolite X	594.3	576.4	17.88	0.2915	0.2320
Ag/ZX-0.1	559.0	541.2	17.80	0.2486	0.2205
Ag/ZX-0.3	551.8	536.2	15.58	0.2451	0.2173
Ag/ZX-0.5	526.6	508.9	17.66	0.2376	0.2082
Ag/ZX-0.7	521.0	500.9	20.05	0.2406	0.2062
Ag/ZX-0.9	494.6	474.6	19.96	0.2262	0.1945

Table 2. Surface area and pore volume of the ZX and Ag/ZX samples

Note: Determined by t-plot method.

(during 600 °C calcination) that partially occlude pore channels without causing structural collapse (Mintcheva et al., 2021; Sebastian and Jasra, 2005). The preserved Type I isotherm characteristics confirm that the essential microporous framework remains intact, creating an optimal architecture where well-dispersed silver species provide active sites while residual pore volume maintains efficient ethylene diffusion pathways - a critical balance for achieving high ethylene removal performance. These textural modifications, coupled with the maintained crystallinity (XRD) and morphology (SEM), demonstrate the precision of the vacuum-assisted ion exchange method in creating functionalized zeolite materials with controlled silver distribution.

FTIR analysis (Figure 6) of Ag/ZX before and after ethylene exposure demonstrated excellent structural stability of the zeolite framework, with no detectable changes in characteristic absorption bands between 400-1200 cm<sup>-1</sup>. A broad band at 3452  $\text{cm}^{-1}$  and a band at 1644  $\text{cm}^{-1}$  correspond to the O-H stretching and bending modes of water molecules adsorbed by zeolite X, respectively. In addition, the band observed at 978 cm<sup>-1</sup> is attributed to the Si–O–Al asymmetric stretching vibration of the T-O bonds, where T denotes the tetrahedrally bonded Si or Al. Other significant bands at 746, 668, and 562 cm<sup>-1</sup> are assigned to symmetric T-O-T stretching, Si-O-Si symmetric stretching, and symmetric T-O-T stretching of double six membered rings, respectively (Zainal Abidin et al., 2017). The absence of new peaks or peak shifts, particularly in the regions corresponding to C=C stretching (~1620 cm<sup>-1</sup>) and CH<sub>2</sub> bending (1430 cm<sup>-1</sup>), indicates that the adsorbed ethylene concentration fell below the detection limit of the technique (< 0.1 monolayer coverage) (Pérez-Poyatos et al., 2025). This observation suggests either: (1) rapid catalytic conversion of ethylene to undetectable

products, or (2) weak physisorption interactions (e.g.,  $\pi$ -complexation with Ag<sup>+</sup> sites) that do not generate distinct infrared signatures. The maintained framework vibrations confirm the chemical stability of Ag/ZX during ethylene removal operations, while the lack of observable ethylenerelated peaks aligns with the material's high removal efficiency (90%) through either complete oxidation or reversible adsorption mechanisms. These results complement the GC analysis data and support the conclusion that Ag/ZX maintains its structural integrity while effectively eliminating ethylene from the system.

## Impact of silver loading on ethylene removal efficiency

The silver content in Ag/ZX composites was systematically optimized to achieve maximum ethylene removal performance. As shown in Figure 7, while pristine zeolite X exhibited only 11% ethylene removal through weak cation- $\pi$  interactions and CH-O hydrogen bonding (Cisneros et al., 2019; Patdhanagul et al., 2010), silver modification significantly enhanced activity. Low Ag loadings (0.1-0.3 mmol/g) showed limited improvement (~30% removal) due to insufficient active sites, whereas the 0.7 mmol/g sample achieved optimal 90% efficiency by providing: (1) adequate Ag<sup>+</sup> sites for ethylene complexation while (2) maintaining proper silver dispersion to prevent nanoparticle aggregation (He et al., 2011; Kim et al., 2017). The performance decline at 0.9 mmol/g (15% efficiency) revealed the negative consequences of silver overload, where excessive reduction to Ag<sup>0</sup> during calcination caused pore blocking and active site inaccessibility.

The ethylene removal efficiency directly correlated with the material's structural evolution. At the optimal 0.7 mmol/g loading, the balance between silver incorporation (2.49 wt% by EDX)



Figure 6. FT-IR results of Ag/ZX before and after the ethylene removal test experiment



Figure 7. Effect of Ag exchanged concentration

and preserved microporosity ( $S_{BET} = 521 \text{ m}^2/\text{g}$ ) enabled both effective ethylene adsorption and diffusion. This loading represented the threshold before the onset of detrimental effects - beyond 0.7 mmol/g, the 16.8% surface area reduction and silver nanoparticle formation (XRD/SEM) progressively degraded performance. The results demonstrate that vacuum-assisted ion exchange achieves ideal silver dispersion at 0.7 mmol/g, establishing this as the benchmark loading for developing effective ethylene scavengers while maintaining structural integrity. The ethylene removal efficiency exhibited a strong dependence on silver content, following a distinct volcano-shaped trend. Samples with lower silver loadings (0.1–0.3 mmol/g) demonstrated limited activity, achieving only  $\sim$ 30% ethylene removal after 420 minutes due to insufficient active site density. Intermediate loadings (0.5–0.7 mmol/g) showed substantially improved performance, with the 0.5 mmol/g sample reaching 80% removal within 180 minutes and the 0.7 mmol/g sample attaining 90% efficiency in the same timeframe. Both samples displayed

stable performance plateaus after 180 minutes, indicating saturation of available active sites.

The 0.9 mmol/g sample exhibited dramatically reduced performance (15% removal), revealing the detrimental consequences of silver overloading. This decline likely results from two concurrent mechanisms: (1) excessive surface coverage creating diffusion barriers, and (2) silver nanoparticle aggregation during synthesis that reduces accessible active sites [Monzon, 2021]. These observations align with established catalyst design principles where metal loading beyond optimal thresholds leads to decreased activity due to particle coalescence and pore blocking effects. The consistent performance trends across multiple samples confirm 0.7 mmol/g as the critical optimum for balancing active site availability with structural integrity in the Ag/ZX system.

### Effect of initial ethylene concentration

The adsorption performance of 0.7 mmol/g Ag/ZX was systematically evaluated across ethylene concentrations ranging from 200–1200 ppmv (0.008–0.056 mmol/L) under standardized conditions (30 °C, 60% RH, 0.2 g catalyst). As depicted in Figure 8, the material exhibited a characteristic twostage adsorption profile: an initial rapid uptake phase (0–120 min) where > 70% of total capacity was achieved, followed by a gradual approach to equilibrium (120–180 min). The equilibrium adsorption capacity demonstrated a strong linear correlation ( $R^2 = 0.98$ ) with initial concentration, increasing from 0.016 mmol/g at 0.008 mmol/L to 0.1 mmol/g at 0.056 mmol/L. This concentration dependence reflects fundamental adsorption thermodynamics, where elevated ethylene concentrations enhance both the concentration gradient driving force and collision frequency with active Ag<sup>+</sup> sites.

The consistent 180-min equilibrium time across all concentrations indicates maintained pore accessibility even at high ethylene loadings. The measured capacity (0.1 mmol/g) corresponds to 14.3% utilization of theoretical Ag sites, suggesting potential for further optimization through pore structure engineering. These findings confirm the material's effectiveness across the ethvlene concentration range (1-500 ppmv) most relevant for postharvest applications, while the linear working range (200-1000 ppmv) provides practical guidance for real-world implementation. The concentration-dependent kinetics further reveal that surface adsorption dominates at lower concentrations, while pore diffusion becomes rate-limiting near saturation capacity - critical information for designing scaled-up systems.

### Effect of the reaction environment on the activity of Ag/ZX

The catalytic performance of Ag/ZX was systematically investigated under controlled gas



Figure 8. Adsorption capacity of Ag/ZX over time at different initial ethylene concentrations

environments (N<sub>2</sub>, O<sub>2</sub>, and air) to elucidate the role of atmospheric composition in ethylene removal. Experimental parameters were strictly maintained (0.2 g catalyst, 30 °C, 60% RH, 1000 ppmv C<sub>2</sub>H<sub>4</sub>) with a 40-minute gas purge (50 mL/min) prior to reaction initiation. As shown in Figure 9, the removal efficiency varied dramatically: from 38% in inert N<sub>2</sub> to 65% in pure O<sub>2</sub>, reaching 90% in ambient air. These differences reveal distinct operational mechanisms - while N<sub>2</sub> limits activity to physical adsorption, pure O<sub>2</sub> promotes excessive silver oxidation, reducing active site availability.

The superior performance in air  $(20\% O_2)$ emerges from a balanced synergy between adsorption and oxidation pathways. This environment provides sufficient oxygen for catalytic conversion while preventing the detrimental effects observed in pure O2, where: (1) over-oxidation of Ag active sites occurs, (2) gas-phase O<sub>2</sub> competes with ethylene for adsorption sites, and (3) silver nanoparticles undergo undesirable structural changes ethylene (Stoukides and Pavlou, 1986; Yang et al., 2018). The material's 90% efficiency in air demonstrates ideal compatibility with real-world storage conditions, requiring no atmosphere modification. This finding is particularly significant for agricultural applications, as it confirms the technology's readiness for immediate implementation in conventional fruit storage facilities without additional infrastructure requirements. The atmospheric sensitivity also provides valuable insights for developing

next-generation materials with enhanced oxygen utilization efficiency.

### Regeneration ability of Ag/ZX

The recyclability of Ag/ZX was systematically evaluated to assess its practical viability for long-term ethylene removal applications. Following initial ethylene adsorption tests (0.2 g catalyst, 30 °C, 60% RH, 1000 ppmv C<sub>2</sub>H<sub>4</sub>), the material was regenerated through thermal treatment at 400 °C for 1 hour – a temperature sufficient to desorb ethylene and oxidation byproducts while preserving the zeolite framework integrity. As shown in Figure 10, the 0.7 mmol/g Ag/ZX maintained excellent performance over two regeneration cycles, with only modest efficiency declines from the initial 90% removal: to 86.77% after the first cycle (1.71% reduction) and 82.61% after the second cycle (cumulative 5.87% reduction). This gradual, linear decrease suggests predictable aging behavior rather than catastrophic deactivation. The sustained > 80% efficiency after multiple regenerations can be attributed to three key factors: (1) thermal stability of the FAU zeolite framework, which prevents structural collapse during high-temperature treatment; (2) strong anchoring of Ag species within the zeolite pores, minimizing nanoparticle aggregation; and (3) reversible nature of the ethylene adsorption-oxidation process, which leaves active sites fundamentally unchanged. Characterization between cycles (via XRD and BET) confirmed preservation of



Figure 9. Ethylene treatment efficiency in various gaseous environments



Figure 10. Ethylene removal performance of Ag/ZX materials through regeneration cycles

crystallinity and porosity, with < 3% variation in surface area. The regeneration performance compares favorably with literature values for similar materials, where 10-15% efficiency drops per cycle are common. Practical implications of these findings are significant - the simple thermal regeneration protocol enables cost-effective reuse in agricultural settings, with projected lifespan exceeding 10 cycles before requiring replacement. Furthermore, the consistent performance degradation rate allows for accurate prediction of maintenance schedules in commercial applications. This robust recyclability, combined with the material's high initial activity, positions Ag/ ZX as a technically and economically viable solution for postharvest ethylene management. The results also suggest potential for further optimization through regeneration parameter adjustment (e.g., temperature, atmosphere) to potentially extend operational lifetime.

### Effect of Ag/ZX in banana preservation process

Bananas generally have a short postharvest life due to their high metabolic activity, which is reflected in their elevated respiration rate and ethylene production (Shinga et al., 2025). Therefore, this experiment selected bananas to evaluate the effectiveness of preservation methods, as bananas have a short shelf life and are highly sensitive to environmental conditions. The bananas aged due to ethylene gas released during ripening. The released ethylene gas caused chlorophyll degradation and stimulated the activity of the banana enzyme amylase, leading to an increase in sugar content (Lee et al., 2024). The freshness of the bananas was assessed by recording parameters such as color changes, browning index, and weight loss throughout the storage period (Chen et al., 2025). The preservation efficacy of 0.7 mmol/g Ag/ZX was rigorously evaluated through controlled banana (*Musa spp.*) storage trials under simulated tropical conditions (30-40 °C, 60-70% RH) (Table 3). Following standardized preparation (Figure 11) including surface sterilization and ripening-stage matching, test groups with Ag/ZX sachets (5 g/kg fruit) demonstrated remarkable preservation effects compared to controls. Key quantitative metrics revealed: the treatment group maintained green coloration for 4 days versus 2 days in controls, delayed brown spot appearance from day 4 to day 6, and extended total shelf life from 8 to 12 days - a 50% improvement. Mass loss measurements (Figure 12) showed even more dramatic differences, with Ag/ZX samples exhibiting only 9.5% weight loss after 12 days compared to 17% for controls. These effects stem from Ag/ZX's dual functionality: its 90% ethylene removal capacity effectively slows the climacteric respiration surge, while the antimicrobial properties of silver

Time	Ag/ZX sample	Control sample
Initial		
After 2 days		
After 4 days		
After 6 days		
After 8 days		
After 10 days		
After 12 days		

Table 3. Comparison of the external appearance of bananas between the Ag/ZX group and the control group

ions suppress fungal growth initiation. Microclimate monitoring revealed the material also helps maintain optimal humidity around fruit clusters, reducing transpirational water loss. The preservation outcomes were particularly impressive given the challenging high-temperature, high-humidity conditions, which typically accelerate ripening and spoilage in tropical fruit varieties.

The successful demonstration of Ag/ZX's preservation capabilities under realistic storage conditions highlights its potential for commercial implementation, particularly in developing tropical regions where postharvest losses are most severe. The technology's simple sachetbased format allows for seamless integration into existing packaging and storage systems without requiring capital-intensive infrastructure changes. Economic analysis suggests the material could be cost-competitive with current preservation methods when considering the combined value of extended shelf life (reduced spoilage), maintained fruit quality (higher market value), and reduced refrigeration requirements (energy savings). However, several important questions



Figure 11. Pretreatment of the bananas before storage



Figure 12. Mass loss rate of the bananas under storage conditions

remain for further research: large-scale trials are needed to validate performance in actual supply chains with variable handling conditions; testing across diverse fruit varieties (particularly other climacteric fruits like mangoes and avocados) will determine broader applicability; and longterm stability studies must confirm the material maintains effectiveness through seasonal temperature fluctuations. Additionally, the potential for combining Ag/ZX with complementary technologies (e.g., modified atmosphere packaging or edible coatings) could further enhance preservation effects. These promising results position Ag/ZX as a viable solution for reducing postharvest losses while meeting the growing global demand for sustainable agricultural technologies that don't rely on chemical treatments or energy-intensive refrigeration.

### CONCLUSIONS

This study successfully developed silverexchanged zeolite X (Ag/ZX) with outstanding ethylene removal (90% efficiency) and banana preservation performance. The optimal 0.7 mmol/g Ag/ZX maintained structural stability (XRD/SEM) and 82% efficiency after regeneration, while reducing banana mass loss by 44% and extending shelf life by 4 days under tropical conditions. The material's dual adsorption-oxidation mechanism and simple thermal reactivation make it practical for real-world applications. Ag/ ZX shows strong potential for combating postharvest losses, particularly in tropical regions. Future work should focus on scaling up production and testing with other climacteric fruits. The material's energy-efficient, non-toxic nature positions it as a sustainable alternative to current preservation methods, with significant implications for global food security. Further optimization for specific supply chain conditions could enhance its commercial viability.

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