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A novel non-iron-based starch, lignin, and halloysite-based oxygen scavenging composite for food packaging applications

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Active packaging technologies are essential for maintaining food quality by reducing oxidative degradation. While iron-based oxygen scavengers are common, concerns regarding safety and sustainability have moved the focus toward bio-based alternatives. In this study, a novel, physically blended bio-based oxygen scavenging system of starch, lignin, halloysite nanoclay (HNC), and calcium carbonate ($CaCO_3$) was developed. The composite was prepared by pre-loading HNC with $CaCO_3$, followed by blending with lignin at varying mass ratios (1 : 0 to 5 : 1) and a constant starch concentration. The incorporation of $CaCO_3$ and HNC was used to overcome the inherent diffusion limitations of dense lignin–starch matrices by creating a more interconnected porous network. The oxygen scavenging potential of the composite was evaluated at three storage temperatures (5 °C, 25 °C, and 60 °C) over 30 days. The results showed clear temperature-dependent behavior; the system was found to be dormant at 5 °C, providing a controlled-activation profile ideal for cold-chain logistics, while exhibiting accelerated kinetics at higher temperatures. Among the formulations, L4H1 demonstrated the highest oxygen-scavenging efficiency, achieving capacities of 7.13 mL O_2 per g at 25 °C and 19.40 mL O_2 per g at 60 °C. Kinetic modeling confirmed zero-order O_2 absorption governed by phenolic site availability, while Arrhenius analysis revealed diffusion-controlled temperature sensitivity. These findings demonstrate the potential of the developed material as an alternative to conventional metallic oxygen scavenger sachets for shelf-stable food packaging applications.

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Sustainability spotlight

This study advances sustainable food packaging through the development of a novel metal-free oxygen scavenging composite based on starch, lignin, halloysite nanoclay, and calcium carbonate. The work eliminates reliance on conventional iron-based scavengers, addressing concerns related to safety and recyclability. Bio-based starch and lignin are utilized as core functional materials, promoting renewable resource use. Lignin valorization adds value to an industrial byproduct in a functional application. Halloysite nanoclay and calcium carbonate enhance porosity and moisture accessibility within the matrix. This improved structure supports efficient activation of lignin's phenolic groups for oxygen scavenging. The system demonstrates effective oxygen uptake under elevated storage conditions. Overall, the composite offers a promising sustainable alternative for active food packaging. The approach supports reduced dependence on petroleum-based and metal-based systems. This work aligns with circular economy principles by promoting waste valorization and material sustainability.

1. Introduction

Active and intelligent packaging are advanced packaging systems designed to improve food quality and safety during storage. Active packaging acts as physical protection for food ingredients and enhances safety by actively interacting with the food's internal environment using scavenging or releasing agents (*e.g.*, oxygen scavengers, antimicrobial agents, and ethylene absorbers) to reduce degradation and spoilage.[1,2] Within active packaging systems, oxygen scavengers are widely used to reduce/eliminate oxygen inside the package and to maintain the sensory and nutritional quality of food by preventing oxidation, off-flavors, and color changes.[3,4] Oxygen scavengers are incorporated directly into the polymer matrix or used as separate components such as sachets, pads, *etc.*[5] Material selection and absorption mechanisms are associated with system efficiency; therefore, biopolymer-based scavengers could offer a more effective, sustainable approach.[1,2] Phenolic compounds, including gallic acid, pyrogallol, and catechins, possess strong antioxidant and oxygen absorption potential up to 595 mg O_2 per g under alkaline and moisture conditions.[6] The hydroxyl groups in phenolic compounds release protons, forming reactive anions that increase oxygen scavenging efficiency.[7] Metal-based systems, *i.e.*, zero-valent iron in cellulose acetate, also remove oxygen and inhibit microbial growth in

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food models.[8] In both cases, the absorption rate is influenced by environmental conditions, polymer compatibility, surface area, and matrix porosity, showing the importance of selecting materials that combine high reactivity with food-safe, structurally supportive matrices.[8]

Traditional iron-based oxygen scavengers are widely used in food and non-food applications; however, ingestion hazards, off-flavor, recycling issues, and consumer acceptance are a few limitations that have driven a shift towards non-iron options. Also, growing awareness of food safety and sustainability has increased the demand for biodegradable and GRAS-certified packaging materials.[9] Non-iron oxygen scavengers are broadly classified into five categories: antioxidants such as ascorbic acid and tocopherols, hydrocarbons like polybutadiene and polyisoprene, enzymatic systems including glucose oxidase and catalase, biological systems such as yeast, and plant-derived polyphenols like gallic acid and catechin.[9] Many studies have investigated various non-iron oxygen scavenger systems, including *Acacia catechu* and calcium carbonate-based oxygen scavengers;[9] natural rubber and PVA-based systems;[10] 3-hydroxyphenol (resorcinol-RC) and potassium carbonate-based moisture-activated oxygen scavengers;[11] polyesters incorporating gallic acid;[12] activated gallic acid;[6] *etc.* Ongoing research into non-iron oxygen scavenger systems continues to expand their potential for safer, more sustainable, and consumer-friendly active packaging applications. The transition of active food packaging from synthetic polymers to bio-based frameworks is growing from laboratory exploration to industrial deployment. Bio-based ecosystem mappings have highlighted that edible films and coatings present a highly transformative path toward circular economies by utilizing agricultural and food processing industry waste. Multinational corporations are scaling bio-based coatings and laminations to minimize plastic pollution and lower carbon footprints. However, implementing these platforms commercially needs to maintain oxygen and water barrier performance, thermal stability, and mechanical strength under dynamic supply chain pressures.[13] An approach of adding mineral fillers into these matrices can establish highly tortuous paths that limit gas permeability and provide specialized, localized active sites for food preservation.[14]

In the present study, a starch, lignin, and HNC–$CaCO_3$ composite was developed as a bio-based oxygen scavenger. This is the first reported composite that combines starch, lignin, HNC, and $CaCO_3$ in a physically blended system to achieve efficient O_2 scavenging while maintaining structural stability. Lignin acted as the primary oxygen-reactive component, with its phenolic groups undergoing moisture-assisted oxidation to consume oxygen within the package headspace. HNC provided nanostructured support to enhance lignin dispersion and increase surface area for O_2 absorption. $CaCO_3$ contributed to microstructural porosity, stabilized pH, facilitated oxygen diffusion, and improved mechanical stability. All components were physically blended, with the starch content held constant while the lignin : HNC–$CaCO_3$ ratios were varied to optimize oxygen scavenging performance. The study offers a sustainable alternative to traditional iron-based oxygen scavengers in active food packaging.

2 Materials and methods

2.1 Materials

Alkaline lignin was procured from Tokyo Chemical Industry Co., Ltd. Starch from Carolina Biological and Halloysite Nanoclay (HNC) and calcium carbonate ($CaCO_3$) was obtained from Sigma-Aldrich. Glass vials (clear borosilicate) equipped with rubber stoppers and plastic–aluminum caps were procured from Four E's Scientific. All chemicals and reagents used in this study were of analytical grade.

2.2 Preparation of the oxygen scavenger

2.2.1 Preloading halloysite with base. HNC (175 g) was dispersed in an amount of deionized water to form a homogeneous slurry. Calcium carbonate ($CaCO_3$) was added at 6 wt% relative to HNC. The slurry was sonicated for 30 minutes to ensure uniform dispersion and promote intimate contact between HNC and $CaCO_3$. The mixture was then dried in an oven at 60 °C until moisture-free. The dried mixture was lightly ground using a mortar and pestle and stored in an airtight container to prevent moisture uptake.

2.2.2 Preparation of the starch binder phase. Starch (200 g) was dispersed in 250 mL of distilled water and heated at 70 °C for 20 minutes for complete gelatinization and uniform hydration. The gelatinized starch was oven-dried at 60 °C followed by grinding to a fine powder and stored in an airtight container. The gelatinized starch acted as a hydrophilic binder and a moisture-responsive phase within the composite matrix, designed to overcome diffusion limitations by creating a porous network that facilitates water transport to the active lignin sites.

2.2.3 Preparation of the lignin–starch–halloysite mixture. Lignin powder and the preloaded HNC–$CaCO_3$ mixture were mixed in varying ratios: 1 : 0 (control), 1 : 1, 2 : 1, 3 : 1, 4 : 1, 5 : 1 (lignin : HNC–$CaCO_3$, w/w). Starch powder was added to

Table 1 Experimental formulations and mass ratios for lignin–starch–HNC oxygen scavenging composites

Sample	Ratio	Lignin (g)	HNC (g)	Starch (g)	Temperature (°C)	Total mass (g)
Control	1 : 0	1	0	0	5, 25, 60	1
L1H1	1 : 1	0.275	0.275	0.45	5, 25, 60	1
L2H1	2 : 1	0.37	0.18	0.45	5, 25, 60	1
L3H1	3 : 1	0.42	0.13	0.45	5, 25, 60	1
L4H1	4 : 1	0.44	0.11	0.45	5, 25, 60	1
L5H1	5 : 1	0.46	0.09	0.45	5, 25, 60	1

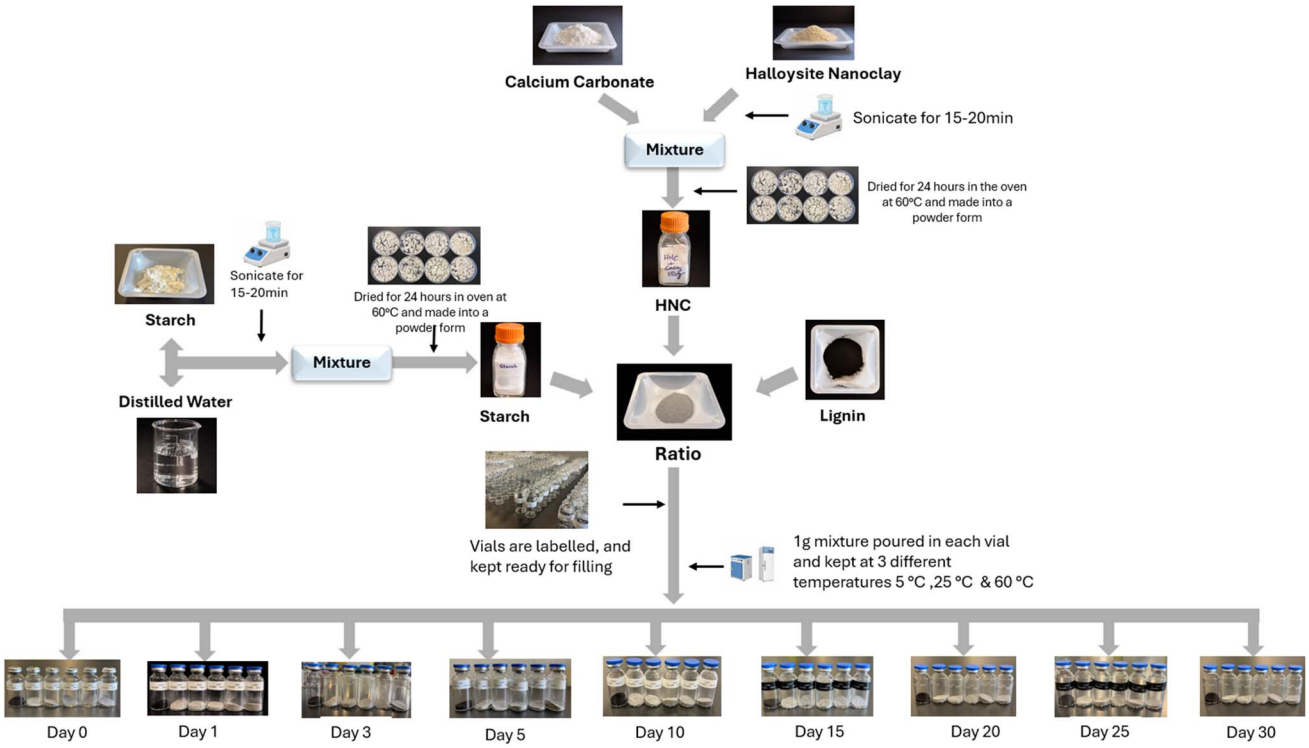

Fig. 1 Overview of the experimental design.

a constant concentration of 0.45 g across all formulations. The total weight of each mixture was maintained at 1 g and the mixture was transferred into clear glass injection vials. Each vial was sealed with a 20 mm aluminum crimp cap with septa using a manual hand crimper to ensure airtight conditions, minimizing moisture and oxygen ingress. Table 1 shows the concentration and ratio of chemicals used to prepare the oxygen scavenger composites. Fig. 1 shows an overview of the process of preparation of oxygen scavenger composites.

2.3 Thermal properties

Thermal properties of the composites were measured using differential scanning calorimetry (DSC), performed on a TA Instruments DSC2500. Briefly, a composite (4.3 mg, db) sample was weighed in an aluminium pan, and distilled water (10 μL) was added using a microsyringe to obtain a suspension. The pan was hermetically sealed and maintained at a constant water-to-composite (70 : 30) ratio, scaled from previously reported DSC preparation steps for starch-based systems (Gu *et al.*, 2024). The samples were equilibrated at room temperature (25 °C) for 24 h before testing. Gelatinization properties were analyzed by heating the starch–water mixture from 20 °C to 120 °C at 10°C min^{-1}. Gelatinization temperatures, including onset (T_o), peak (T_p), and conclusion (T_c), and enthalpy change (ΔH) were analyzed using TA universal analysis software (TA Instrument, USA).

2.4 Oxygen scavenging evaluation

2.4.1 Storage conditions. The effect of storage temperature on the oxygen scavenging potential of the prepared composites was measured. All samples with varying lignin-to-HNC ratios (1 : 0, 1 : 1, 2 : 1, 3 : 1, 4 : 1, and 5 : 1) were subjected to different temperatures: 5, 25, and 60 °C. Refrigeration conditions (5 °C) were maintained by placing the samples in a temperature-controlled refrigerator with a digital display. To avoid fluctuations in ambient conditions, room temperature (25 °C) was simulated by storing the samples in a controlled oven set at 25 °C. An elevated temperature (60 °C) was applied using a hot air oven to accelerate oxygen-related reactions. This temperature was selected to simulate accelerated aging conditions, as higher temperatures increase the rate of oxidation and formation of reactive oxygen species, allowing for rapid evaluation of the oxygen scavenger's performance under accelerated oxidative conditions. A total of 432 bottles were filled and sealed. All vials were equilibrated for 30 min before the first measurement to stabilize internal headspace conditions.

2.4.2 Headspace oxygen measurement. Headspace oxygen concentration was measured using a gas analyzer (Gas Advance GS3 Micro, Illinois Instruments). The sampling needle was inserted through the septum, and oxygen concentration (%) was recorded at each time point. The instrument was calibrated using ambient air prior to each measurement.

2.5 Calculation of oxygen scavenging performance

2.5.1 Oxygen scavenging capacity. Oxygen scavenging capacity (mL O_2 per g) was calculated using the reduction in oxygen concentration between the initial and final measurement points

$$O_2 \text{ capacity } (\text{mL g}^{-1}) = \frac{V_c \times [\%O_2(i) - \%O_2(f)]}{100 \times m} \quad (1)$$

where V_c = vial volume (mL), m = mass of the material (g), $\%O_2(i)$ = initial oxygen concentration in the vials (20.9% v/v at $t = 0$ days), and $\%O_2(f)$ = final oxygen concentration at time t.

2.5.2 Oxygen scavenging rate. The oxygen scavenging rate was calculated as the change in oxygen capacity over time:

$$R = \frac{O_2 \text{ capacity}}{t} \quad (2)$$

where R is expressed as mL O_2 per g per day and t is the time (days).

The rate represents the average oxygen consumption per unit time over the selected interval.

2.6 Kinetic modeling

Oxygen scavenging kinetics were analyzed using a zero-order kinetic model, which assumes that the rate of oxygen absorption is constant and independent of the headspace oxygen concentration.[15]

$$C_t = C_0 - kt$$

Here, C_t = oxygen concentration at time t, C_0 = initial oxygen concentration, and k = zero-order rate constant.

2.7 Arrhenius and activation energy analysis

The temperature dependence of the rate constant was evaluated using the Arrhenius equation:

$$k = A\, e^{-E_a/RT} \quad (3)$$

where E_a = activation energy (J mol^{-1}), R = universal gas constant (8.314 J mol^{-1} K^{-1}), T = absolute temperature (K), and A = pre-exponential factor.

Activation energy was determined from the slope of the linearized form:

$$\ln k = \ln A - \frac{E_a}{R} \cdot \frac{1}{T} \quad (4)$$

2.8 Statistical analysis

Using R (version 4.3.0) through RStudio, an analysis of variance (ANOVA) was carried out on the data for the experimental results. A significance level of $P < 0.05$ was used to determine statistical significance.

3. Results and discussion

3.1 Thermal analysis

The thermal stability and phase transition behavior of the developed composite matrix were evaluated using differential scanning calorimetry (DSC). DSC runs were conducted for L3H1 and L4H1 formulations, which were identified during preliminary screening as optimized compositions. Specifically, L3H1 was selected for the highest scavenging performance, whereas L4H1 was selected for the upper limit of filler loading to define the thermal stability range of the developed system.

The DSC behavior of the two best-performing formulations, L3H1 and L4H1, was characterized by using DSC over the temperature range of 0 to 300 °C. Both formulations exhibited a multi-staged thermal profile comprising three distinguishable regions: (i) a broad endothermic region from 50–150 °C, (ii) a transition zone around 150–200 °C, and (iii) an exothermic event beyond 200 °C (Fig. 2). In DSC thermograms of composite biopolymer systems, first-order transitions are observed as well-defined peaks, while second-order transitions manifest as variations in the heat flow baseline. At higher temperatures, oxidative decomposition and thermal degradation events are typically observed as exothermic peaks.[16] Both L3H1 and L4H1 showed broad, shallow endothermic features between 50 and 150 °C, consistent with the removal of physically adsorbed and structurally bound moisture from the composite matrix. For lignin-containing materials, a characteristic endothermic peak around 110 °C has been documented, attributed specifically to the removal of physically absorbed water held within the lignin structure through hydrogen bonding with its abundant hydroxyl group.[17] In starch–nanoclay composites, an endothermic peak around 115 °C is similarly attributed to the elimination of interlaminar water located between the nanoclay layers, a phenomenon characteristic of HNC-incorporated biopolymer systems.[18] For the starch-based films more broadly, two endothermic peaks are commonly reported, one around 65 °C and another around 114 °C, corresponding to plasticizer-mediated moisture interactions and crystalline reorganization within the starch matrix, respectively.[19]

In L3H1 and L4H1, the depth shows the endothermic nature of that region rather than a sharp peak, which reflects the composite character of the system, where moisture is distributed across multiple components, the starch, lignin, and HNC lumen and $CaCO_3$ particles each releasing bound water at slightly different temperatures. The overlapping of these individual desorption events produces the broad endothermic profile observed in both formulations.

Beyond 150 °C, both formulations showed an exothermic transition in the range of approximately 200–270 °C, which is associated with the onset of thermal oxidative degradation of the organic components within the composite. Lignin undergoes thermal oxidative degradation through cleavage of aryl-ether bonds and benzene ring structures, producing phenolic aldehydes and carboxylic acid intermediates in a process that is exothermic in nature.[20] The starch-based composite thermal degradation onset was reported at 260 °C, with a maximum decomposition rate near 300 °C, consistent with the thermal transitions shown in the present study.[21] L3H1 showed a slightly broader and more pronounced exothermic peak than L4H1, with a wider heat flow range, which suggests that the higher lignin to HNC ratio in L3H1 contributes to greater thermal reactivity at high temperatures. Whereas L4H1 showed a subdued thermal profile, which seemed more stable due to the interaction of lignin, HNC and $CaCO_3$ at the L4H1 ratio, which is consistent with its oxygen scavenging potential.

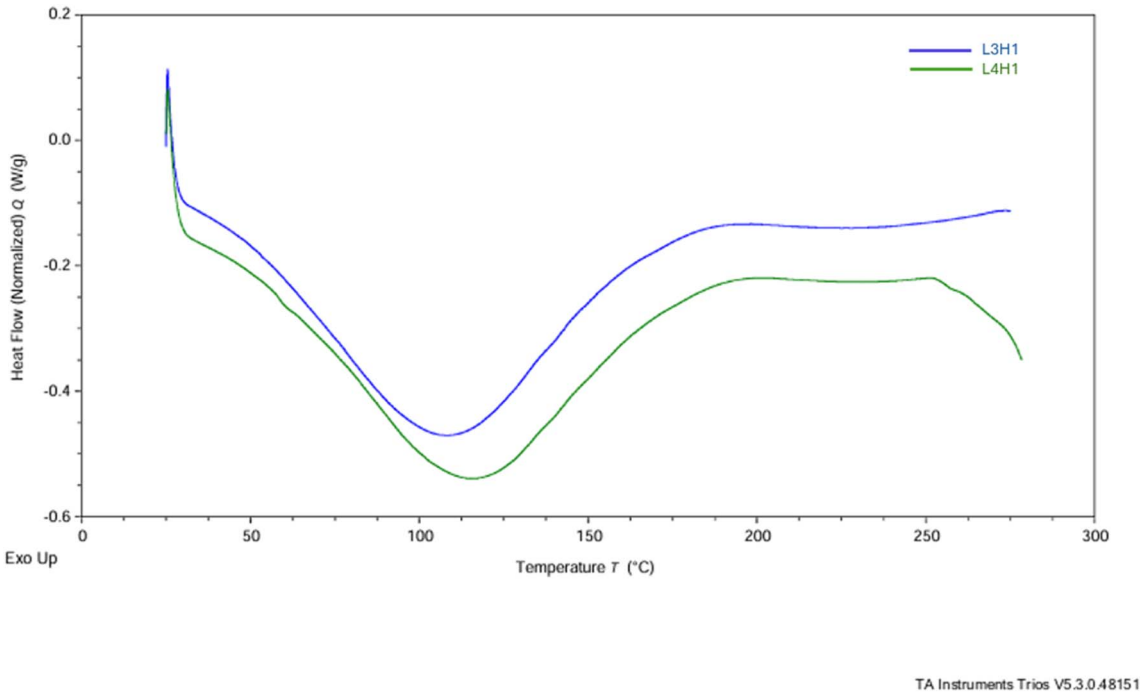

Fig. 2 DSC graphs of L3H1 and L4H1.

The ability of both formulations to remain thermally stable below 200 °C is relevant to food packaging, confirming that neither formulation undergoes premature thermal degradation under typical processing or storage conditions.

3.2 Oxygen scavenging potential

The oxygen scavenging behavior of the developed composites was consistent with the mechanism reported for moisture-activated biopolymer-based scavenging systems. Upon exposure to moisture, $CaCO_3$ formed a mild alkaline microenvironment within the gelatinized starch matrix and promoted the activation and reduction of oxygen into reactive oxygen species (ROS).[22] The gelatinized starch phase functioned as a moisture-responsive network that helped in water absorption and diffusion throughout the composite and helped with the initiation of oxygen-scavenging reactions at internal active sites. Lignin served as the principal electron donor and underwent oxidation through interaction with the activated oxygen species, resulting in the formation of quinone-type structures. The observed temperature-dependent scavenging kinetics, particularly the accelerated oxygen uptake at 60 °C relative to 5 °C, further support a moisture-assisted and diffusion-controlled reaction pathway. These findings demonstrate that the starch–lignin–HNT–$CaCO_3$ system effectively regulated oxygen scavenging performance and reaction kinetics within the developed composite system.[23]

3.2.1 Effect of storage conditions and concentration on oxygen scavenging activity. The initial oxygen concentration in the vials was 20.9%, which corresponds to atmospheric equilibrium conditions before activation of the oxygen scavenging system. Upon exposure to different temperatures of 5 °C, 25 °C, and 60 °C, the developed lignin–starch–HNC-based oxygen scavenger exhibited a clear temperature-dependent scavenging behavior. The initial concentration decreased to 15.2% and 5.38% by day 30 at 25 °C and 60 °C, respectively. It was observed that at 60 °C, the developed oxygen scavenger works comparatively faster than at 25 °C. The samples stored at 5 °C didn't show any effect on the oxygen inside the vials, indicating strongly temperature-dependent reaction kinetics and limited activation of oxidative functional groups at low temperature. Composite dormancy at 5 °C acts as a built-in 'pause button' to preserve or maintain the scavenger's full efficiency until the product encounters ambient conditions where oxygen control is actually needed.

The effect of concentration on oxygen scavenging capacity and the rate of development of the oxygen scavenging system was studied. Starch concentrations were kept constant, whereas the concentration of lignin–HNC–$CaCO_3$ was varied. It was observed that the samples kept at 25 °C and 60 °C showed a significant reduction, whereas the samples kept at 5 °C didn't show any reduction in the headspace oxygen. The absence of oxygen scavenging activity at 5 °C represented a temperature limitation of the developed system under refrigeration conditions. This behavior could be due to the high activation energy (E_a) barrier required for the oxidation of lignin-derived phenolic structures. At lower temperatures, the reduced molecular mobility and limited water diffusion within the starch matrix may limit matrix swelling and restrict the proton-transfer pathways required to generate reactive phenoxyl radicals. Consequently, the scavenging mechanism becomes significantly suppressed under chilled storage conditions. Although this restricts the applicability of the material for refrigerated

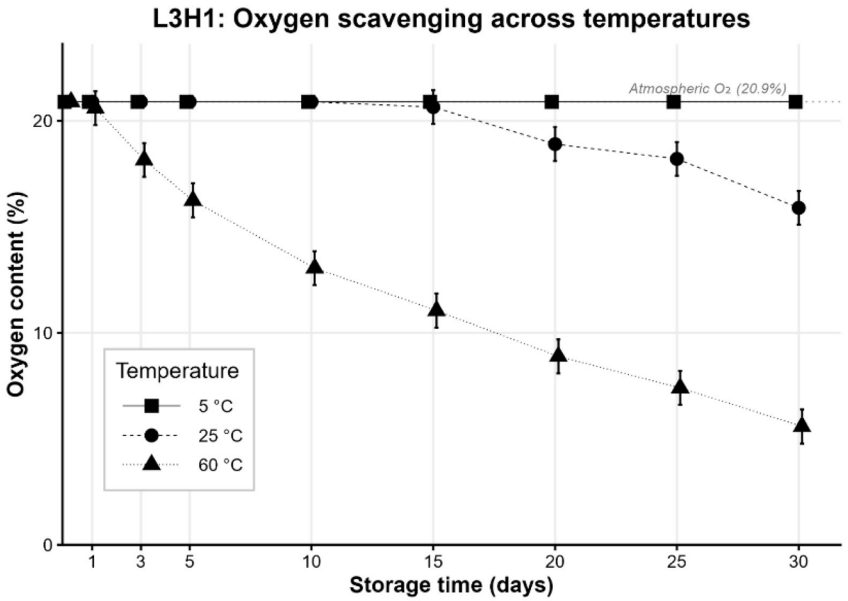

Fig. 3 Oxygen scavenging L3H1 (lignin : HNC; 3 : 1) at 5, 25, and 60 °C.

food products such as fresh meat and seafood, the observed temperature sensitivity may also provide a practical advantage during the storage and handling of the packaging material itself. Particularly, decreased activity at low temperature could minimize premature oxygen consumption during refrigerated storage, transportation, or processing before package sealing.

Furthermore, the scavenging capacity at 60 °C was evaluated as an accelerated kinetic profiling technique to quickly reach maximum saturation for mathematical model validation, rather than simulating actual food storage conditions. At the realistic storage temperature of 25 °C, the composite exhibits a controlled, sustained scavenging response (achieving a capacity of 7.13 mL O_2 per g by day 30) that is highly compatible with the shelf-life requirements of ambient, dry, or intermediate-moisture foods, such as bakery items or powdered nutritional goods, where trace residual oxygen mitigation is necessary.

Among all the ratios of lignin and HNC–$CaCO_3$ concentrations, L3H1 and L4H1 showed a significant reduction in headspace oxygen. It was also observed that L4H1 showed 10.53% and 17.75% greater reductions than L1H1 at 25 °C and 60 °C, respectively. The concentration of lignin affects the oxygen

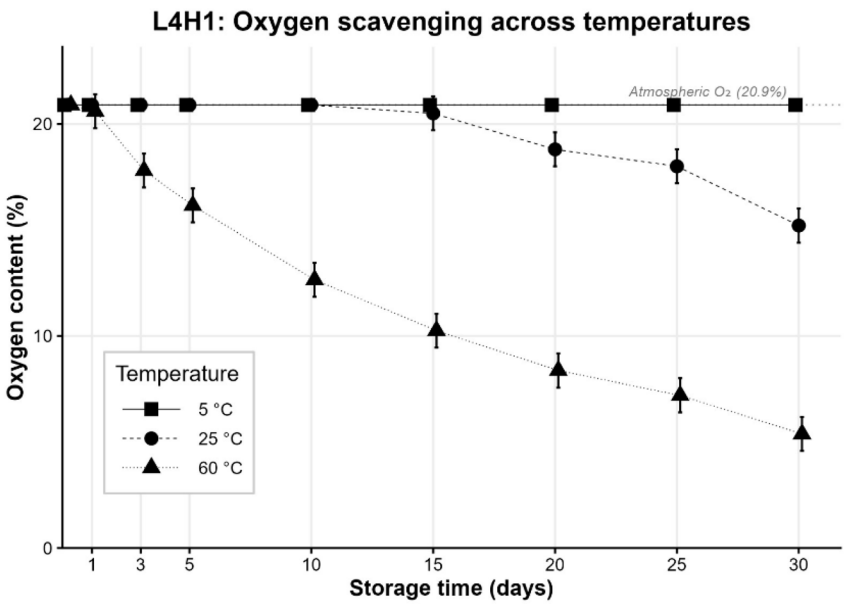

Fig. 4 Oxygen scavenging L4H1 (lignin : HNC; 4 : 1) at 5, 25, and 60 °C.

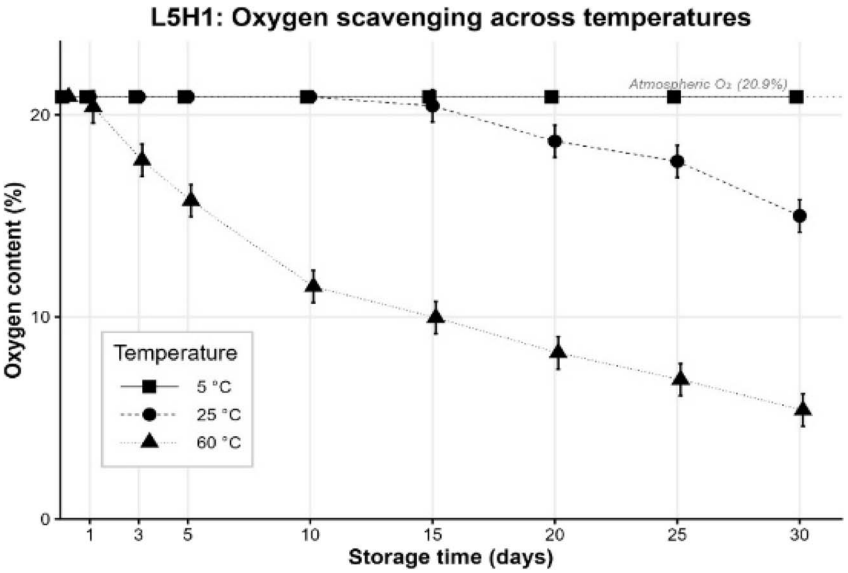

Fig. 5 Oxygen scavenging L5H1 (lignin : HNC; 5 : 1) at 5, 25, and 60 °C.

scavenging capacity; as we increase the concentration of lignin, the oxygen scavenging capacity also increases.

To clarify the contribution of each component and verify the importance of the multi-component design, a series of control formulations were examined during the early stages of material development. Individual components, including lignin, HNC, and $CaCO_3$ alone, were unable to form cohesive self-supporting matrices under the same solution-casting conditions. In addition, starch–lignin control systems prepared without the incorporation of HNC and $CaCO_3$ exhibited either negligible or substantially delayed oxygen scavenging behavior.

The limited scavenging performance observed in the starch–lignin system is likely associated with strong intermolecular hydrogen bonding between starch and lignin chains, resulting in a compact polymer network with restricted free volume. This dense chain system could reduce moisture penetration and limit oxygen diffusion toward the phenolic hydroxyl groups responsible for scavenging potential. Whereas, adding a rigid HNC framework loaded with $CaCO_3$ significantly altered the matrix architecture by disrupting polymer chain packing and promoting the formation of localized voids and interconnected diffusion pathways. These structural modifications facilitated improved transport of moisture and oxygen within the

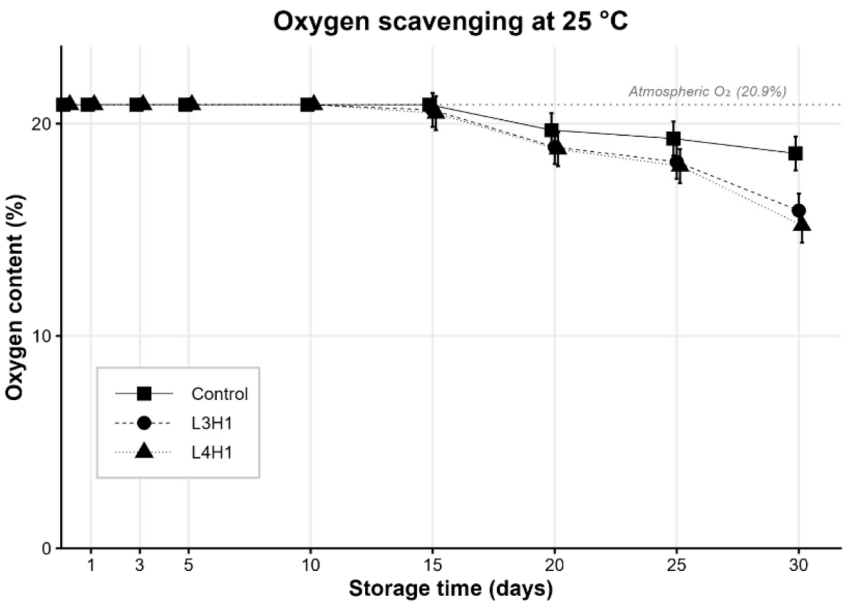

Fig. 6 Oxygen scavenging activity of the control (lignin : HNC; 3 : 0), L3H1 (lignin : HNC; 3 : 1) and (lignin : HNC; 4 : 1) at 25 °C.

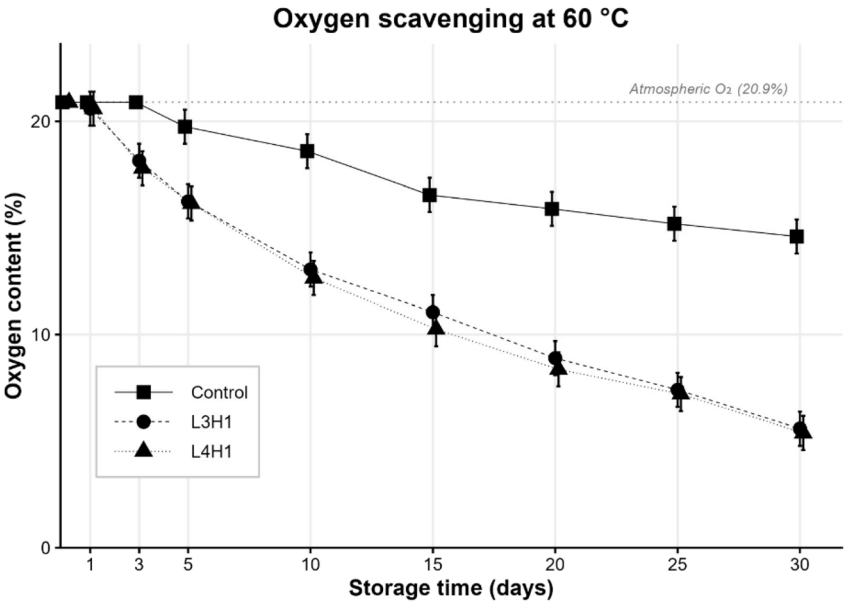

Fig. 7 Oxygen scavenging activity of the control (lignin : HNC; 3 : 0), L3H1 (lignin : HNC; 3 : 1) and (lignin : HNC; 4 : 1) at 60 °C.

composite, thereby enabling effective activation of the scavenging mechanism. The comparative analysis of the control formulations, therefore, highlights the critical structural role of the HNC/$CaCO_3$ phase in achieving functional oxygen scavenging performance (Fig. 3–7).

3.2.2 Oxygen scavenging capacity and rate. The oxygen scavenging capacity and rate of the lignin/starch/HNC composite system were calculated using eqn (1) and (2). Among all formulations, L4H1 demonstrated the highest oxygen scavenging capacity, 7.13 mL O_2 per g at 25 °C and 19.40 mL O_2 per g at 60 °C at the final storage point (30 days), with corresponding oxygen scavenging rates of 0.238 and 0.647 mL O_2 per g per day, respectively (Table 2). The increase in both the capacity and rate at higher temperatures is consistent with Arrhenius-type kinetics, where higher temperatures accelerate the rate of oxidative reactions and enhance the phenolic radical activity. A comparable trend was observed for an *Acacia catechu*–$CaCO_3$ based oxygen scavenging system, which demonstrated capacities of 10 ± 1.13 mL O_2 per g and 15.56 ± 0.51 mL O_2 per g at 25 °C and 60 °C, respectively, with rates of 0.50 ± 0.05 and 0.77 ± 0.02 mL O_2 per g per day, and where rate constant values increased with rising temperatures.[15] These results collectively demonstrate that the L4H1 formulation exhibits consistent and temperature-responsive oxygen-scavenging performance, supporting its potential as a bio-based, biodegradable active packaging material.

This behavior can be attributed to the increased mobility of reactive species and the increased rate of oxidation of phenolic structures in lignin at higher temperatures. The oxygen scavenging mechanism is primarily governed by the oxidation of phenolic hydroxyl groups in lignin, which generate phenoxy radicals capable of reacting with molecular oxygen, thereby reducing headspace oxygen levels. High temperature likely accelerates both radical formation and diffusion-controlled oxygen transport within the matrix, leading to faster scavenging kinetics.

The observed trend is consistent with the general Arrhenius-type temperature dependence of oxidation reactions in bio-based active packaging systems, where the reaction rate increases exponentially with temperature due to reduced activation energy barriers and improved molecular mobility within polymeric networks. Similar temperature-responsive oxygen depletion behavior has been previously reported in lignin- and polyphenol-based active packaging systems, where oxidation of phenolic moieties governs oxygen uptake dynamics.[24] Furthermore, variation in lignin and HNC–$CaCO_3$ concentrations significantly influenced scavenging performance. All formulations stored at 25 °C and 60 °C exhibited measurable oxygen depletion; however, samples L3H1 and L4H1 demonstrated the highest oxygen reduction efficiency at both temperatures. This suggests a strong concentration-dependent scavenging mechanism, where increased lignin content provides a higher density of accessible phenolic hydroxyl groups, thereby enhancing radical generation and oxygen consumption capacity.

This trend is consistent with previous findings showing that lignin's oxygen scavenging activity and antioxidant activity increase with the availability of phenolic hydroxyl groups capable of donating hydrogen atoms and stabilizing free radicals.[25] In addition, lignin-based active systems in starch and biopolymer matrices have been shown to exhibit enhanced oxygen scavenging performance due to increased radical-mediated oxidation reactions and improved interfacial accessibility of reactive sites.[26] Additionally, the incorporation of nano-hybrid $CaCO_3$ structures likely contributes to improved dispersion and increased interfacial area, facilitating oxygen diffusion pathways and enhancing contact between oxygen molecules and reactive lignin sites. The synergistic interaction between lignin, starch matrix, and nanostructured fillers

Table 2 Calculated oxygen scavenging capacity (mL O_2 per g) and rate (mL O_2 per g) for optimized formulations

Concentrations	O_2%	Temperature	Day	Capacity (mL O_2 per g)	Rate (mL O_2 per g)
L3H1	20.7	25	15	0.25	0.017
L3H1	18.9	25	20	2.50	0.125
L3H1	18.2	25	25	3.38	0.135
L3H1	15.9	25	30	6.25	0.208
L4H1	20.5	25	15	0.50	0.033
L4H1	18.8	25	20	2.63	0.132
L4H1	18	25	25	3.63	0.145
L4H1	15.2	25	30	7.13	0.238
L3H1	11.2	60	15	12.13	0.809
L3H1	8.96	60	20	14.93	0.747
L3H1	7.4	60	25	16.88	0.675
L3H1	5.58	60	30	19.15	0.638
L4H1	10.1	60	15	13.50	0.900
L4H1	8.36	60	20	15.68	0.784
L4H1	7.2	60	25	17.13	0.680
L4H1	5.38	60	30	19.40	0.647

therefore plays a critical role in modulating both the kinetics and extent of oxygen scavenging. This is consistent with the enhanced performance observed in L3H1 and L4H1 formulations, which benefit from optimized filler distribution and improved accessibility of reactive functional groups.[27,28]

While the oxygen absorption capacity of the lignin–HNT–$CaCO_3$ system is competitive with bio-based alternatives, it provides a functional balance specifically tailored for sensitive, bio-based food applications. High-capacity chemical scavengers often suffer from rapid kinetic depletion and potential migration issues. Our composite is engineered as a long-term, moisture-gated preservative; by utilizing the HNC–$CaCO_3$ architecture to modulate reactivity, we prioritize a sustained, stable scavenging rate over high-volume, short-burst absorption.

3.3 Kinetic modeling and activation energy analysis

Two distinct aspects of the scavenging kinetics were evaluated: (i) the order of the reaction with respect to headspace O_2 concentration, and (ii) the temperature-sensitivity of the rate constant itself. These reflect different steps in the overall scavenging pathway and are not expected to share a single rate-limiting mechanism.

For (i), the oxygen scavenging kinetics were analyzed using a zero-order kinetic model, which assumes that the rate of absorption is constant and independent of the oxygen concentration in the headspace. While the scavenging process in diffusion-limited biopolymer matrices can exhibit non-linear depletion, the zero-order model provided a strong fit to the experimental data, with average coefficients of determination of $R^2 = 0.98$ for L3H1 and $R^2 = 0.99$ for L4H1 across the tested temperatures, confirming its validity for describing the primary scavenging phase in this system. This indicates that O_2 consumption is constant and independent of headspace O_2 concentration, consistent with a system in which the rate-limiting step is the finite population of reactive phenolic hydroxyl sites available for oxidation at a given time, rather than the concentration of O_2 remaining in the headspace: once sites are activated, the reaction proceeds at a rate set by site availability, not by how much O_2 is left to react with them. For (ii), the temperature-dependent kinetics of the optimized formulations, L3H1 and L4H1, were evaluated using the Arrhenius equation to determine E_a. The rate constants (k) increased significantly as temperature rose from 25 °C to 60 °C, consistent with Arrhenius-like behavior. This trend aligns with established kinetics for phenolic oxygen scavengers, where the activation energy for gallic acid-based bio-based multilayer packaging films was reported to be 75.4 kJ mol^{-1}, substantially higher than the 44.1–49.0 kJ mol^{-1} range documented for commercial iron-based scavengers, indicating greater temperature sensitivity in phenolic systems relative to iron-based ones. Supporting this, pyrogallol-based systems have similarly shown oxygen scavenging capacity increasing substantially with temperature, with reported values of 6.8 mL, 50.4 mL, and 209.6 mL at 5 °C, 23 °C, and 60 °C, respectively, at 99% RH.

The E_a values observed in our study for L3H1 and L4H1 formulations were 26.84 kJ mol^{-1} and 23.51 kJ mol^{-1}, respectively. These values fall within the 20–30 kJ mol^{-1} range typical of diffusion-controlled processes in biopolymer matrices, indicating that the magnitude of k is governed by how readily O_2 physically diffuses through the starch-based network to reach the encapsulated lignin. This is not in conflict with the zero-order result above: site saturation determines the functional form of the rate law (zero-order in O_2 concentration at a fixed temperature), while diffusion through the matrix determines how that rate law's pre-factor changes with temperature. The two findings describe different links in the same reaction chain. These results indicate that our composite architecture effectively mitigates the excessive temperature sensitivity often associated with natural polyphenols. The structural modulation of the starch–lignin matrix provides a more favorable thermodynamic profile, ensuring consistent and controlled performance for ambient food packaging applications without the extreme temperature-induced fluctuations reported in earlier

natural phenolic composite models. The lower E_a observed for the L4H1 composite compared to L3H1 serves as quantitative evidence of the 'diffusion paradox' resolution within this quaternary system. While higher lignin loading typically increases matrix density and creates tortuous paths for gas molecules, the synergistic inclusion of HNC and $CaCO_3$ at the 4 : 1 ratio appears to counteract this effect. By creating a more interconnected microporous network, these fillers lower the energetic barrier for molecular oxygen to reach the reactive phenolic sites. This confirms that the nanostructured mineral phase is indeed pivotal in overcoming the inherent diffusion limitations of dense lignin–starch matrices, effectively providing a 'faster' pathway for oxygen scavenging as evidenced by the reduced E_a.

The absence of scavenging activity at 5 °C can be thermodynamically explained by the E_a; at refrigeration temperatures, the available thermal energy ($RT = 2.3$ kJ mol^{-1}) is insufficient to overcome the energy barrier required for phenolic radical formation and subsequent oxygen consumption. Furthermore, the decrease in E_a for L4H1 compared to L3H1 provides quantitative evidence of the synergistic effect between the lignin and the nanostructured fillers. The inclusion of HNC and $CaCO_3$ likely increases the free volume and creates preferential diffusion pathways, thereby reducing the energy required for oxygen molecules to penetrate the composite and react with the active phenolic hydroxyl groups.

4. Commercial implications and design considerations

The scientific novelty of this composite lies in its moisture-gated activation mechanism, which shifts oxygen scavenging from passive, continuous oxidation to a controlled, triggered response. Within this architecture, the starch matrix acts as a structural gate, while halloysite nanotubes (HNTs) provide a unique confinement effect that prevents lignin aggregation, ensuring optimal radical scavenging accessibility. Concurrently, the incorporated $CaCO_3$ establishes an alkaline microenvironment that lowers the activation energy of the lignin–oxygen reaction. By integrating these specific components, the system remains dormant under ambient storage and activates precisely in response to environmental spoilage triggers, offering a level of controlled reactivity and shelf-life stability that is superior to conventional random-blend systems.

From a commercial perspective, our starch–lignin–HNT–$CaCO_3$ system is designed for operational stability. Its dormancy at 5 °C acts as a built-in 'pause button,' preserving the scavenger's full potential until the product encounters ambient conditions where oxygen control is actually needed. We recognize that this dormancy limits immediate protection within strictly refrigerated environments. However, this temperature-sensitive behavior is a deliberate design choice, as it ensures that the material remains fully active for shelf-stable goods that are most vulnerable to oxidation during retail or ambient display. For applications requiring active protection throughout the entire cold chain, we envision future iterations of this composite where the starch matrix or lignin-to-HNC ratios are adjusted to lower the activation energy, effectively tuning the trigger temperature to meet specific industrial requirements.

Regarding the storage stability of the starch–lignin–HNT–$CaCO_3$ composite, this composite exhibits robust shelf-life characteristics due to the low moisture sensitivity of the crystalline starch domains at ambient humidity (RH < 50%). Unlike high-reactivity iron-based scavengers, our composite's 'dormancy' mediated by restricted mobility within the starch matrix, allows for handling under standard dry-storage conditions. To guarantee maximum performance, we recommend storage in moisture-barrier materials, such as metallized oriented polypropylene (OPP) or aluminum-laminated pouches. This simple secondary packaging effectively isolates the composite from environmental humidity, ensuring that the scavenger retains its activity profile until integrated into the final food packaging architecture.

Furthermore, while the current architecture is optimized for low-to-intermediate moisture foods, future work involving cross-linking of the starch binder could further broaden its utility for higher-moisture environments. When applying such technology, it is essential to recognize that oxygen scavenging effectiveness is inherently tied to the specific deterioration pathways of the target food. While a strong correlation exists between oxygen depletion and reduced lipid oxidation in items such as roasted nuts and meat emulsions, scavengers are not a universal solution. For instance, in dairy products where photo-oxidation is the primary degradation mechanism, or in scenarios where specific residual oxygen thresholds are required to maintain meat color, the scavenger must be carefully tuned to avoid adverse effects like off-flavors or premature souring.[29,30] Our lignin–HNT–$CaCO_3$ system addresses these concerns by offering a non-iron, food-safe alternative that minimizes the potential for the secondary chemical side effects often associated with reactive metallic scavengers.

The functional efficacy of our composite aligns with the broader shift toward plant-derived antioxidant systems in active packaging. As highlighted by Eranda *et al.*[31] (2024), utilizing agricultural by-products is vital for a circular food economy, reducing reliance on fossil-fuel-based packaging. Furthermore, the development of edible films and coatings doped with plant extracts represents a critical frontier in the biopreservation of high-protein foods like fresh tuna.[32] Their review emphasizes that for such systems to be commercially viable, they must successfully manage the complex interactions between the film matrix and the food's internal biochemistry. Recent research, such as the study by Eranda *et al.*[33] demonstrates that natural polyphenols are highly effective at modulating the redox transitions of myoglobin in muscle foods. While plant extracts primarily function *via* direct radical scavenging and interaction with heme proteins to preserve color and stability, our lignin-based composite operates as a complementary strategy by managing the headspace oxygen concentration. Together, these approaches represent a comprehensive, bio-composite paradigm for food preservation, where plant extracts stabilize the internal biochemistry of the food and our oxygen-scavenging

scaffold provides the external environmental control necessary to prevent oxidative degradation at the source.

5. Conclusion

This study successfully demonstrated the fabrication of a bio-composite, non-iron oxygen scavenger based on a quaternary blend of starch, lignin, HNC, and $CaCO_3$. Among the developed formulations, L4H1 emerged as the optimal composite, balancing lignin-derived reactive functionality with a porous mineral–nanostructured framework to achieve an oxygen scavenging capacity of 7.13 mL O_2 per g at 25 °C and 19.40 mL O_2 per g at 60 °C over 30 days. The temperature-dependent scavenging behavior, characterized by an activation energy of 23.51 kJ mol^{-1} for L4H1, confirms the thermally activated nature of phenolic oxidation within the lignin matrix. Notably, the composite remained dormant at 5 °C, with no measurable oxygen depletion observed under refrigeration conditions; this temperature-gated activation profile distinguishes the system from continuously reactive scavengers and offers a practical advantage for cold-chain handling, where premature oxygen consumption before package sealing is undesirable.

The synergistic effect between the nanostructured halloysite and alkaline $CaCO_3$ creates a micro-environment that effectively lowers the energy barrier for phenolic radical formation. Furthermore, the absence of metallic components is expected to reduce the risk of off-flavors and support compatibility with industrial metal detection systems. Future work will focus on the integration of this composite into flexible film structures for commercial-scale food packaging validation. Ultimately, this research provides a foundation for a scalable and sustainable pathway for utilizing industrial lignin by-products in high-value active packaging applications.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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