Innovative eco-friendly active packaging strategy aimed for ethylene removal

David Ruperez[1], Nicolás Gracia[1], Cristina Nerín[1], Filomena Silva[1,2,3]

[1] Grupo Universitario de Investigación Analítica (GUIA), Departamento de Química Analítica
Instituto de Investigación en Ingeniería de Aragón (I3A)
Universidad de Zaragoza, Mariano Esquillor s/n, 50018, Zaragoza, Spain.
Tel. +34-976762707, e-mail: druperez@unizar.es
[2]Agencia Aragonesa para la Investigación y el Desarrollo (ARAID)
[3]Facultad de Veterinaria, Universidad de Zaragoza, Miguel Servet 177, 50013, Zaragoza, Spain.

Summary

Within the scope of sustainability, this work tackles both food waste and food safety by studying the ethylene scavenging potencial of α-cyclodextrin nanosponges produced by solvent-free synthesis and the food safety evaluation of the compostable packaging for food contact applications where the nanosponges will be incorporated.

Introduction and aim

Every year, over one third of all fresh fruits and vegetables are lost before they reach the consumers (1). Ethylene produced by fruits and vegetables accelerates ripening and consecuently, food spoilage (2), creating the need for safe ethylene removal approaches in order to control ripening and increase the shelf-life of packaged produces. Some of the most studied ethylene scavengers for food packaging contain potassium permanganate or heavy metals (palladium) that, due to their toxicity, cannot be in direct contact with foods and pose a real safety challenge when disposed. In addition, the European Union is leading towards biodegradable or bio-based packaging over traditional ones, in order to overcome the rising environmental concerns caused by plastic materials. Thus, new eco-friendlier materials and new ethylene scavengers are needed. Cyclodextrin nanosponges (CD-NS) are novel and innovative cross-linked cyclodextrin polymers virtually nontoxic, organic and biodegradable, with much higher pH and temperature stability when compared to their monomer counterparts. These properties together with their gas carrier potential (3) make these polymers very attractive to be used in sustainable food packaging, although their application in the field is not exploited yet.

The present study aims to develop new active packaging for fruit that can tackle both fruit waste and food safety of new sustainable packaging by incorporating cyclodextrin nanosponges as ethylene removal approach into a compostable packaging material.

Materials and methods

A solvent-free α-CD-NS synthesis was applied to α -cyclodextrin and carbonyldiimidazole at a 1:4 (CD:CDI) molar ratio on a PM 100 planetary ball mill, and the CD-NS products characterized using Fourier-transform infrared spectroscopy (FTIR). To fully extract the potentially toxic unreacted imidazolyl carbonyl groups, CD-NS were washed with water using different temperatures (40 and 70 ºC), and agitation speeds, and with ultrasonic extraction. Extraction efficiency was monitored over 8 hours by targeting imidazole using a validated liquid chromatography coupled to a diode array detector (HPLC-DAD).

Ethylene absorption experiments were performed by exposing CD-NS, zeolite and bentonite powders to ethylene standards in air (10 ppm). Ethylene concentration was determined using gas chromatography (GC) coupled to a flame ionization detector (FID).

Migration studies on a series of different biopolymer films were performed according to EU regulation 10/2011. Migration of volatile and non-volatile substances into the food simulants was then analysed by liquid chromatography coupled to high resolution mass spectrometry (UPLC-QTOF) and solid phase micro-extraction gas chromatography coupled to mass spectrometry (SPME-GC-MS).

Results and discussion

CD-NS were successfully synthesized, scaled-up and characterized using FTIR giving a high yield (99%). Purification experiments suggest that all theoretical imidazolyl carbonyl groups are extracted after 6 hours of extraction with water at 40 ºC, with no significant differences between ultrasonic assisted extraction and agitation on a water bath, as confirmed by HPLC-DAD and nitrogen elemental analysis. The HPLC-DAD analytical method targetting imidazole was validated, achieving low limits of detection (3ppb) and quantificacion (10ppb). Ethylene absorption experiments showed that CD-NS have a clear tendency as an effective ethylene scavenger when compared to commercial zeolites and bentonites. No significant changes were observed between day 3 and 4, suggesting that an absorption equilibrium is reached after 72 hours. After demonstrating their potential for ethylene removal, these compounds were included by extrusion in biodegradable films. Migration studies revealed a high migration of non-volatile polyester oligomers from the blank films, making these films potentially unsafe as food contact materials and not suitable for incorporating CD-NS.

Conclusions

Due to their biological origin, biodegradability, stability and non-toxicity, CD-NS can be considered an ideal candidate to be incorporated into novel packaging films aimed for ethylene removal, as they have demonstrated their ability to scavenge this gas. However, the biopolymer films evaluated in this study did not comply with food safety requirements and their manufacture should be further modified in order to increase their safety and be able to use them for CD-NS incorporation. Overall, the in vitro results showed that CD-NS can be effectively scaled-up and used to develop an ethylene removal active packaging for fruits.

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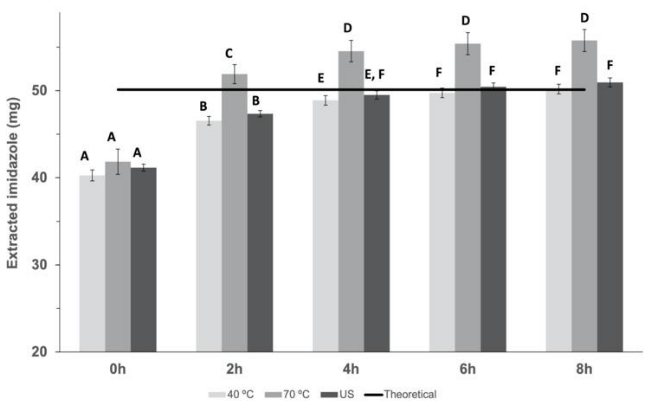

Figure 1: Results of the amount of imidazole extracted across time at 40 ºC and 70 ºC under constant stirring and ultrasonic extraction. Mean ± SD of three replicates is shown and compared against the theoretical imidazole in the samples. Different letters show significant differences (p≤0.05) between samples.

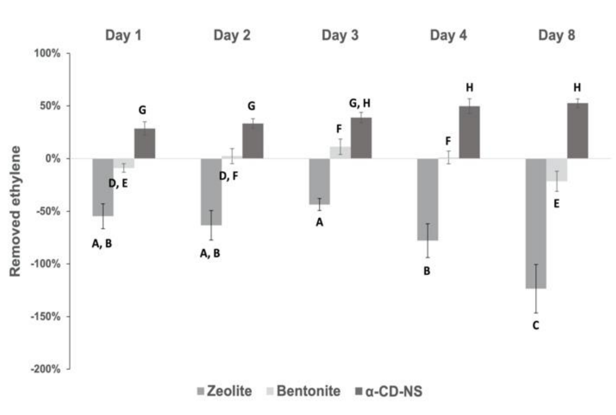

Figure 2: Ethylene removal percentage of α-CD-NS and commercial bentonite and zeolite across time. Mean ± SD of three replicates is shown. Different letters show significant differences (p≤0.05) between samples.