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Antioxidant activity of coatings containing eugenol for flexible aluminium foils to preserve food shelf-life

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ABSTRACT

Active food packaging is an innovative system that avoids food deterioration ensuring quality, safety and shelf-life extension of food. Herein, two novel eugenol vinyl-based resins were used for coating flexible aluminium foils with potential packaging applications. Coatings were prepared with single eugenol or loaded eugenol in Santa Barbara Amorphous15 (SBA-15) mesoporous silica nanoparticles, and their antioxidant activity was investigated by DPPH, ABTS, ORAC, TBARS assays and by the hydroxyl free radicals' generator method with HPLC analysis. Antioxidant activity was also evaluated exposing the coatings to various food simulants. Both coatings revealed adequate antioxidant capacity when exposed to fatty food simulants and to vapour phase hydroxyl free radicals (scavenging > 50%). The incorporation of eugenol in SBA-15 reduced its release to 65%, promoting eugenol beneficial antioxidant effects over time. The release of eugenol from the coatings into food simulants is not required for the activity of free radical scavenging.

1. Introduction

Food waste has become a major concern for the global food security and the food industry, causing significant negative implications for the environment in terms of resources used (e.g., water, soil, etc.), loss of terrestrial biodiversity and global greenhouse gas emissions. Every year, food is lost or wasted from harvesting to retail market reaching an overall quantity of 89 million tonnes in Europe (Alves et al., 2022) due to spoilage processes and to shelf-life expiration. Food deterioration is strongly affected by numerous intrinsic (e.g., water activity, pH, redox state, nutrient content) and extrinsic (e.g., atmospheric gases, temperature of storage, moisture) factors. Organic compounds such as carbohydrates, proteins, and lipids in food, are mainly involved in spoilage phenomena due to oxidative processes or deterioration by microorganisms, leading to the loss of food nutritional and organoleptic values, as well as inevitably reducing food shelf-life.

Oxidative processes may occur during food production, storage, processing and preparation stages (Mozuraityte et al., 2016) and can mainly affect proteins and polyunsaturated fatty acids, which represent a salient issue (Ahmed et al., 2016) since lipid oxidation leads to the formation of toxic aldehydes, responsible for unpleasant food tastes and odours (Jamróz & Kopel, 2020). Light, transition metals, certain enzymes (e.g., lipoxygenase) and several compounds in food (e.g., chlorophylls, riboflavin, porphyrins, pheophytins, and bilirubin) can catalyse the autoxidation of lipids when they react with oxygen or can promote the production of free radicals (Nerín, 2010). A valid and emerging strategy to improve the quality of food avoiding oxidative processes and extension of shelf-life, is represented by Active Food Packaging (AFP). This approach provides safer and healthier foods to the consumers by overcoming the typical features of traditional food packaging. According to the EU Regulations 1935/2004, 450/2009, active packaging consists of deliberate incorporation of active substances either into packaging headspace or within the packaging material (Nerín et al., 2017). To date, various active packaging systems have been developed (absorbent/scavenging activity vs free radicals, O_2, CO_2, ethylene, humidity; release/emission of antioxidants and antimicrobials) (Yildirim et al., 2018), but are currently under investigation with few active packaging materials on the market, due to difficulties

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encountered at an industrial scale or for its inappropriateness for food contact. Antioxidant (AO) releaser systems involve both synthetic (e.g., butylated hydroxy anisole, butylated hydroxytoluene, *tert*-butylhydroquinone and propyl gallate) and natural antioxidants. The use of natural compounds (e.g. essential oils, EOs), especially those present in herbs and spices, would avoid potential adverse effects on human health caused by some synthetic molecules (Jamróz & Kapel, 2020).

EOs such as those of rosemary clove (*Syzygium aromaticum* L.), (*Rosmarinus officinalis* L.), cinnamon (*Cinnamomum zeylanicum* L.), ginger (*Zingiber officinale* Rosc.), oregano (*Origanum vulgare* L.), and their main aromatic compounds are well known for their AO properties (Borzi et al., 2019; Wicochea-Rodríguez et al., 2019; Song et al., 2020; Wrona et al., 2021) and can be used as natural active food additives according to the Food and Drug Administration (FDA) and to EU Regulation. European Commission, 2008. Eugenol (EG) is the main EO component in cloves, cinnamon, allspice and basil and its use for food contact materials has been established by the EU Regulation (10/2011). EG is known for numerous biological mechanisms including anti-inflammatory, anticancer, antiviral, antifungal, antibacterial, and antioxidant properties (Ulanowska & Olas, 2021). These latter are related to its ability to scavenge free radicals or to inhibit lipid peroxidation (Gülçin, 2011; Orlo et al., 2021; Chen et al., 2023a).

An innovative approach has recently captured scientific and industrial attention, represented by the encapsulation of active natural compounds (i.e., EO) into porous inorganic nanocarriers to allow the controlled release of the antimicrobials/antioxidants and their protection toward UV and/or solvents, enhancing the packaging material efficiency for an overall improvement in food quality (Tescione et al., 2014; Bahrami et al., 2020).

In the present work, in vitro investigations were performed on the antioxidant activity of two new vinyl formulations containing either EG or EG loaded in Santa Barbara Amorphous15 (SBA-15) mesoporous silica nanoparticles (MSN) to coat flexible aluminium foils for potential food packaging applications. SBA-15 mesoporous silica, developed by researchers at the University of California at Santa Barbara and characterized by hexagonal pores that feature a narrow pore-size distribution and a pore diameter from 5 nm to 15 nm, was used as a nanocarrier. Its high hydrothermal and mechanical stability, its ability to embed active molecules in its internal porosity for both preservation of specific activity and control of release by pore architecture, pore size and specific molecule/pore wall interactions encourage its use (Stanzione et al., 2017; Verma et al., 2020). Furthermore, when compared to other mesoporous silicas, SBA-15 contains pores with a larger diameter which permits accommodation of a greater quantity of molecules (Zhang et al., 2021). The advantage of using SBA-15 MSN is its adequateness as an inorganic support, owing to its uniform wide channels that immobilize organic molecules. Its stability ensures improved biocompatibility, dispersion, and functionalization (Guntero et al., 2017).

The aforementioned new formulations had been previously studied by Orlo et al. (2023) who performed in-depth experimental characterization, presented in terms of chemical structure, specific surface area, corrosion resistance, surface wettability and antibacterial activity. To the best of our knowledge, current literature indicates the use of eugenol and active compounds in low density polyethylene (LDPE), polyethylene terephthalate, polylactic acid (Sanahuja & García, 2021), starch-based films (Chen et al., 2023b). Aluminium is among the most used packaging materials due to its several characteristics like its excellent corrosion temperature resistance, lightness, high mechanical strength, high ductility, barrier efficiency against gases, moisture and light, as well as its high recyclability (Doğan et al., 2009) although studies are lacking regarding the antioxidant efficacy of eugenol-based aluminium active food packaging.

Herein, in an attempt to better our knowledge concerning the properties of the vinyl-based coatings, we firstly assessed their AO activity by exposing them directly to $DPPH^{\bullet}$ methanol and $ABTS^{\bullet+}$ aqueous solutions. Subsequently, AO activity was also indirectly evaluated exposing the coatings to various food simulants (10% ethanol for aqueous foods, 3% acetic acid for acidic foods, 50% ethanol for medium lipophilic foods, and 95% ethanol for fatty foods) for 1, 3 and 7 days at refrigeration (5 °C) and room temperatures (25 °C). Then, the AO activity of eugenol released from the coatings was assessed in terms of radical scavenging and inhibition of lipid peroxidation by DPPH, ABTS, ORAC and TBARS assays. This approach could be suited for potential target foods to package and for studying changes in their AO activity related to temperature and time of exposure. Finally, the radical scavenging efficacy of the coatings that were not exposed to food simulants was tested using an in-situ hydroxyl free radicals' generator and results were analysed via HPLC with fluorescence detection, which enabled investigations concerning the potential of the materials to scavenge free radicals present in the packaging headspace.

2. Material and methods

2.1. Reagents

Eugenol (purity ≥ 99%, CAS: 97–53–0), Silica mesoporous Santa Barbara Amorphous15 (CAS: 7631–86–9), ethanol (CAS: 64–17–5), acetic acid (CAS: 64–19–7) 2,2-diphenyl-1-picrylhydrazyl (DPPH, CAS: 1898–66–4), potassium persulfate (CAS: 7727–21–1), 20-azino-bis (3-ethylbenzothiazoline-6-sulfonic acid) diammonium salt (ABTS, CAS: 30931–67–0), 2-thiobarbituric acid (TBA, CAS: 504–17–6), trichloroacetic acid (CAS: 76–03–9), Tween 80 (CAS: 9005–66–7), tannic acid (CAS:1401–55–4), rapeseed oil (CAS: 8002–13–9), tris hydrochloride (CAS: 1185–53–1), 2,20-azobis(2-methylpropionamidine) dihydrochloride (AAPH, CAS: 2997–92–4) and fluorescein (CAS: 518–47–8) were supplied by Sigma-Aldrich (Milano, Italy).

2.2. SBA-15 impregnation with eugenol

SBA-15 was impregnated with eugenol (Orlo et al., 2023). The procedure is briefly reported in Supplementary Material.

2.3. Active coating preparation

A solvent-based vinyl resin (VIN) was supplied by Laminazione Sottile S.p.A. (San Marco Evangelista, Italy), generally used to coat flexible aluminium foils (Al) for food contact. No detailed information is reported regarding the resin due to patent secrecy.

The vinyl resin was used to design two coatings for aluminium flexible foils (12 μm thick) obtaining 10 ± 2 g polymer/m^2 aluminium foil. Specifically, the two coatings were: (i) coating containing 5% EG (5 g EG per 100 g of vinyl resin mas); (ii) coating containing a combination of 2.5% EG (2.5 g EG per 100 g of vinyl resin mass) and 2.5% EG loaded in SBA-15 (2.5 g EG loaded in SBA-15 per 100 g of vinyl resin mass), thus with a total mass of eugenol corresponding to 5%. The two samples were respectively coded as Al/VIN/5%EG and Al/VIN/5%EG/SBA-15. Details of the procedure are reported in the previous work (Orlo et al., 2022). The two formulations were stirred at 1200 rpm for 30 min. Methyl ethyl ketone (MEK) was used to regulate viscosity to facilitate the distribution of resin on the aluminium foil. Then, each active formulation and pristine resin were cast onto aluminium foils using a bar coater (K101 CONTROL COATER, by URAI, Italy, characterized by a spreadable surface of 170 ×250 mm and a variable speed range of 2–15 m/min). The coated aluminium samples were dried for 20 s at 80 °C. After drying, the desired coating value was 10 ± 2 g/m^2 of aluminium foils. To verify this value, a 10 cm × 10 cm sample was weighed before and after the removal of the coating using MEK. Resin removal was performed by scrubbing the coated aluminium.

2.4. Antioxidant activity of active coatings

2.4.1. Screening of the antioxidant activity

Antioxidant activity of Al/VIN/5%EG and Al/VIN/5%EG/SBA-15 was screened by measuring their radical scavenging activity by DPPH and ABTS assays described below. Radical scavenging percentage (RS%) was calculated in reference to the neat (Al/VIN) polymer according to Orlo et al. (2021).

2.4.1.1. DPPH assay. The DPPH assay was performed in line with Brand-Williams et al. (1995). Pieces (0.19 cm^2) of neat, Al/VIN/5%EG and Al/VIN/5%EG/SBA-15 coatings were placed in quadruplicate in 96-well microtiter plates and 235 μL of $DPPH^{\bullet}$ methanol solution (101.43 μM) was added. After 30 min the materials were removed, and the absorbance was recorded at 515 nm. Radical scavenging activity (RS) was calculated in percentage as follows:

$$RS\% = \left[\frac{ODnegative \quad control - ODsample}{ODnegative \quad control}\right] \times 100 \tag{1}$$

2.4.1.2. ABTS assay. The ABTS assay was conducted according to Lavorgna et al. (2021). $ABTS^{\bullet+}$ was prepared by co-incubating ABTS aqueous solution (7 mM) with $K_2S_2O_8$ aqueous solution (140 mM) for 16–18 h in the dark. The $ABTS^{\bullet+}$ solution was firstly diluted with phosphate buffer solution to obtain 0.7 ± 0.02 OD (734 nm) and then 227 μL of the radical solution was placed in contact with neat, Al/VIN/5%EG and Al/VIN/5%EG/SBA-15 polymeric coatings (0.19 cm^2) in quadruplicate in 96-well microtiter plates. After 6 min, the materials were removed and the absorbance was recorded at 734 nm. RS (%) was calculated according to Eq. (1).

2.5. Antioxidant release test

Release studies of eugenol from Al/VIN/5%EG and Al/VIN/5%EG/SBA-15 coatings were carried out by determining its migration from the polymer into 10% ethanol (aqueous food simulant), 3% acetic acid (acidic food simulant), 50% ethanol (medium lipophilic food simulant) and 95% ethanol (fatty food simulant) after 0, 1, 3 and 7 days at 5 °C and 25 °C.

Release tests were performed as follows: a 3 cm^2 piece of each polymeric sample and 5 mL of food simulant (area-to-volume ratio 6 dm^2/L) were placed in glass vials and covered to avoid eugenol photodegradation. The concentration of eugenol in each food simulant was analysed by UV spectroscopy at the different selected times and quantified using an absorbance/concentration (mM) calibration curve of eugenol. The antioxidant efficacy of eugenol concentrations in the food simulants was tested using DPPH, ABTS, ORAC and TBARS assays.

2.5.1. Determination of DPPH and ABTS radicals scavenging activity

The $DPPH^{\bullet}$ and $ABTS^{\bullet+}$ scavenging ability of the food simulants, that had been in contact with Al/VIN, Al/VIN/5%EG and Al/VIN/5%EG/SBA-15 was determined according to Lavorgna and co-authors (2019) and Orlo and co-workers (2022). In detail, 15 μL of food simulants were tested in quadruplicate with 235 μL of $DPPH^{\bullet}$ solution (101.43 μM) in DPPH assay and 22.7 μL of food simulants were tested with 227 μL of $ABTS^{\bullet+}$ solution (7 mM) in ABTS assay. The absorbance was read at 515 nm after 30 min in DPPH assay and at 734 nm after 6 min in ABTS assay. RS (%) was calculated using Eq. (1).

2.5.2. Determination of oxygen radical absorbance capacity (ORAC)

The ORAC assay was carried out following the procedure of Gillespie et al. (2007). The oxygen radical absorbance capacity (AUC_{net}) of the food simulants in contact with Al/VIN, Al/VIN/5%EG and Al/VIN/5%EG/SBA-15 was determined. In detail, 25 μL of each food simulant was added to 150 μL of fluorescein (80 nM) in 96-well microtiter black plates. After a co-incubation for 10 min at 37 °C, 25 μL of AAPH (150 mM) was added. A blank containing only fluorescein and AAPH was also prepared. Fluorescence decay (λex = 485 nm, λem = 525 nm).

was registered for 55 min every 5 min. The area under the fluorescence decay curve (AUC) was determined as follows:

$$AUC = (0{\cdot}5 + F5/F0 + F10/F0 + F15/F0 + \cdot\cdot + Fn/F0) \times 5 \tag{2}$$

F0 represents the fluorescence reading at time 0 while Fn represents the fluorescence reading at time n.

Starting from AUC of blank and AUC of samples, the AUC net was calculated according to the following formula:

$$AUCnet = AUCsample - AUCblank \tag{3}$$

2.5.3. Determination of thiobarbituric acid reactive substances (TBARS)

The TBARS assay was performed according to procedures defined by Sroka and Cisowski (2003). TBARS represents markers of lipid peroxidation, formed during irradiation with UV light (254 nm) of an oily emulsion added with food simulants. In detail, 30 mL of reagent A (30 mg of tannic acid and 375 mg of thiobarbituric acid dissolved in 30 mL of hot water) was mixed with 70 mL of reagent B (15 g of trichloroacetic acid dissolved in 70 mL of 0.3 M HCl) to obtain TBA reagent. Then, emulsion was prepared by adding 5.2 μL of rapeseed oil to a solution containing 15.6 mg of Tween-40 dissolved in 2 mL of Tris-HCl (0.2 M, pH 7.4). The emulsion was irradiated with UV light (254 nm) for 1 h and then 100 μL of each food simulant was added to 1 mL of it and the mixture was irradiated for 30 min (254 nm). Irradiated samples were mixed with 2 mL of TBA and placed in a boiling water bath for 15 min. Subsequently, the samples were centrifuged at 1500 g for 3 min and the supernatant was measured at 532 nm. The percentage of inhibition of lipid peroxidation (ILP%) was calculated in reference to a blank according to the following equation:

$$ILP\ (\%) = [(OD\ negative\ control - OD\ sample)/(OD\ negative\ control)] \times 100 \tag{4}$$

2.6. Hydroxyl free radicals' generator

Pezo et al. (2006, 2007, 2008) developed a method for producing hydroxyl free radicals (OH·) in situ, which was used to evaluate the antioxidant potential of developed active films. To conduct the experiment, a PA/LDPE bag (12 × 12 cm) with a micropipette tip inlet and outlet was prepared for each sample, and the sample (1 dm^2) was inserted. The OH·generator was then connected to the bag inlets. Blanks (neat polymer, 1 dm^2) were used as controls. A quartz tube reaction chamber was used for irradiation with UV light and an aqueous solution of hydrogen peroxide (0.29 M) was added to generate the radicals. The OH·radicals were then captured using 50 g of an aqueous solution of sodium salicylate (2 μg/g, pH = 4.5) in amber bottles for 24 h. The main product thereby generated, was the fluorescent compound 2,5-dihydroxybenzoic acid, which resulted from the reaction of sodium salicylate with the free radicals. Analysis was then conducted on the main product using high-performance liquid chromatography (HPLC) with fluorescence detection. The samples were injected directly into a Waters HPLC Alliance 2795 Separation module (Milford, MA, USA), which was coupled to a Waters 474 Scanning Fluorescence Detector. The excitation and emission wavelengths used were 324 and 448 nm, respectively. Chromatographic separation was achieved using Waters Atlantis™ dC18 column and mobile phase (10% methanol and 90% acetic/acetate buffer (35 mmol/L, pH = 5.9)) set at a flow rate of 1 mL/min. Isocratic mode was applied. Injection volume was 10 μL. Column and sample temperature was maintained at 25 °C.

2.7. Data analysis

For each assay, three independent experiments, with at least four replicates each, were performed. Radical scavenging (%), inhibition of lipid peroxidation (%), AUC_{net} values and hydroxylation (%) were analysed by Prism 5 analysis (GraphPad Inc., USA) to obtain the mean and the standard deviation. Hydroxylation percentages determined by testing the two active materials were statistically compared to that of the neat coating using one-way Anova-Dunnett's multiple comparison test (***$p < 0.0001$), while one-way Anova-Tuckey's multiple comparison test was used to determine the significant difference for $p < 0.05$ among the active coatings.

3. Results and discussion

3.1. Screening of the antioxidant activity of coatings

A preliminary screening related to the antioxidant capacity of Al/VIN/5%EG and Al/VIN/5%EG/SBA-15 was performed by exposing them to $DPPH^{\bullet}$ and $ABTS^{\bullet+}$ solutions. The results, reported in Table 1 and expressed as RS %, were calculated in reference to the neat coating (Al/VIN).

Both active coatings were able to scavenge the DPPH radical by more than 50%, demonstrating high effectiveness. The solubilisation of eugenol in radical solutions plays a key role in determining its AO activity to permit a more efficient extraction of eugenol on behalf of the $DPPH^{\bullet}$ methanol solution due to the lipophilic property of eugenol compared to the $ABTS^{\bullet+}$ aqueous solution (very low $ABTS^{\bullet+}$ scavenging % was registered). The material containing eugenol (approximately 0.5 g/m^2 of aluminium foil) showed a higher efficiency in scavenging the $DPPH^{\bullet}$ compared to the material containing eugenol loaded in SBA-15 nanocarrier, most likely due to the low eugenol release determined by the carrier.

Similar results were obtained by Navikaite-Snipaitiene et al. (2018) who developed polypropylene films coated by cellulose acetate additivated with eugenol (0.44 ± 0.09 g/m^2) causing 60% inhibition of the DPPH radical after 30 min of incubation. Moreover, it is noteworthy to compare the scavenger activity obtained by Al/VIN/5%EG in this work to that of eugenol as pure molecule studied by Orlo and collaborators (2021) who observed that EG was able to scavenge the DPPH radical by 50% at 0.152 mM. Herein, DPPH radical scavenging of 81.53% was obtained at solubilized EG concentration ≤ 0.246 mM, related to each aluminium foil tested (0.19 cm^2) with 9.5 μg EG/235 μL $DPPH^{\bullet}$ methanol solution, suggesting that when EG is present in Al/VIN/5%EG, its activity is almost equal or higher compared to its function regarding pure EG.

3.2. Antioxidant activity of the released EG

DPPH radical scavenging effect is related to the amount of eugenol released, thus release studies of eugenol from the coatings were conducted by exposing them to food simulants according to the EU legislation (10/2011) (3% acetic acid, 10%, 50% and 95% ethanol) for 0, 1, 3 and 7 days at 5 °C and 25 °C. Timing and temperature were crucial to establish whether the release kinetics of the phytochemical was impacted. Eugenol release was monitored using spectrophotometric analysis and its migrated concentrations are reported in Table 2.

When Al/VIN/5%EG/SBA-15 was exposed to the food simulants, a lower amount of migrated eugenol was recorded compared to that migrated from Al/VIN/5%EG. These results highlighted that the SBA-15 nanocarrier was able to decrease the eugenol release up to 65% (obtained comparing 0.0216 vs. 0.0619 mM, in Table 2) after 7 days of exposure to 50% ethanol at 5 °C, demonstrating the potential use of 5% EG/SBA-15 to preserve food shelf-life for a longer time. At 25 °C, after 7 days of exposure, SBA-15 nanocarrier reduced the eugenol release to 30% and 38%, respectively at 50% and 95% EtOH. Pazos et al. (2016) studied the α-tocopherol migration from chitosan films and affirmed that the migrations of phytochemicals from coatings is facilitated at 25 °C, in line with this study, thus implying the predictable key role of temperature in the release of phytochemicals. Furthermore, the data in Table 2 clearly exhibits the highest eugenol migration occurring in 50% and 95% EtOH simulants. López-de-Dicastillo et al. (2010, 2011) incorporated the flavonoids quercetin, catechin and the green tea extracts into polymeric matrices containing a copolymer of ethylene-vinyl alcohol and studied their release to alcoholic and aqueous simulants, encountering higher migrations to 95% ethanol, presumably due to the better solubility of the flavonoids and green tea extracts in this food simulant.

The present study demonstrates the ability of the nanocarrier SBA-15 to decrease the eugenol release mainly at 5 °C, extending the shelf-life of fatty foods. In parallel, the antioxidant efficiency of eugenol concentrations (from Al/VIN/5%EG and Al/VIN/5%EG/SBA-15) was measured by testing the aliquots of food simulants containing the phytochemical using DPPH, ABTS, ORAC and TBARS assays to better understand the different aspects of antioxidant capacity of the two coatings studied. Figs. 1 and 2 show the antioxidant activity results.

The antioxidant activity of both coatings was higher in the $ABTS^{\bullet+}$. After 7 days of exposure of Al/VIN/5%EG to 50% ethanol the radical scavenging percentages reached more than 30% and 70% at 5 °C and 25 °C, respectively, while for the same coating exposed to 95% ethanol at both temperatures for the same time, the RS percentage was equal to 80%. As regards Al/VIN/5%EG/SBA-15, the ABTS radical scavenging of approximately 30% and 70% after 7 days of exposure to 95% ethanol at 5 °C and 25 °C, respectively was determined. The AUC_{net} values obtained from ORAC assay and ILP obtained from TBARS showed the lowest antioxidant activity of both active coatings in all simulants exposed to both temperatures.

Although eugenol concentrations migrated at the refrigeration conditions, the concentrations were lower than those migrated at 25 °C (Table 2), but still able to exert antioxidant activity. Several studies have reported that active materials work at refrigeration temperature. Echeverría et al. (2018) effectively studied films with soy protein isolate-montmorillonite containing clove essential oil in the conservation of bluefin tuna fillets at refrigeration temperature. Torrieri et al. (2011) proposed the combination of modified atmosphere and antioxidant active packaging containing α-tocopherol. A low rate of oxidation in the fresh fillets of the bluefin tuna after 18 days of storage at 3 °C was reported on application of the combined system.

Our investigations demonstrated efficiency of SBA-15 in slowing down the release kinetic of eugenol. Nevertheless, an antioxidant activity ($ABTS^{\bullet+}$ scavenging equal to 28.58% and 64.68% after 7 days of exposure to 95% ethanol at 5 °C and 25 °C, respectively) was achieved demonstrating the potential application of the material containing the carrier to avoid possible oxidative damage occurring in food stored on a long-term basis. The science of nanomaterial is currently of great interest and the use of nanocarriers, to promote a controlled release of active compounds over time has certainly improved the applicability of bioactive-encapsulated films/coating, ensuring the shelf-life stability of food systems (Chaudhary et al., 2017; Liu et al., 2018). Heirlings et al. (2004) investigated the antioxidant activity of LDPE and ethylene vinyl acetate containing α-tocopherol and α-tocopherol adsorbed onto SBA-15 MSNs, to ensure a controlled release during the shelf-life of the food

Table 1
DPPH and ABTS radical scavenging activity. $DPPH^{\bullet}$ and $ABTS^{\bullet+}$ scavenging activity (%) ± standard deviation (n = 3) recorded by Al/VIN/5%EG and Al/VIN/5%EG/SBA-15.

	Radical scavenging %	
	$DPPH^{\bullet}$	$ABTS^{\bullet+}$
Al/VIN/5%EG	81.53 ± 0.80	1.37 ± 1.83
Al/VIN/5%EG/SBA-15	65.64 ± 1.52	6.63 ± 0.71

Table 2
Eugenol migrated concentrations. Concentrations (mM) of eugenol migrated from Al/VIN/5%EG and Al/VIN/5%EG/SBA-15 into 3% acetic acid, 10%, 50% and 95% ethanol (EtOH), after exposure for 0, 1, 3 and 7 days (D) at 5 °C and 25 °C. Mean ± standard deviation (n = 3) were reported.

Coating	T °C	Time	[mM]			
			10% EtOH	3% Acetic Acid	50% EtOH	95% EtOH
Al/VIN/5%EG	5 °C	D 0	0.0000 ± 0.0000	0.0000 ± 0.0000	0.0000 ± 0.0000	0.0000 ± 0.0000
		D 1	0.0013 ± 0.0000	0.0020 ± 0.0001	0.0110 ± 0.0004	0.0474 ± 0.0019
		D 3	0.0015 ± 0.0004	0.0024 ± 0.0001	0.0245 ± 0.0021	0.0743 ± 0.0004
		D 7	0.0015 ± 0.0001	0.0024 ± 0.0003	0.0619 ± 0.0010	0.1294 ± 0.0217
	25 °C	D 0	0.0000 ± 0.0000	0.0000 ± 0.0000	0.0000 ± 0.0000	0.0000 ± 0.0000
		D 1	0.0019 ± 0.0001	0.0029 ± 0.0003	0.0313 ± 0.0005	0.0715 ± 0.0123
		D 3	0.0071 ± 0.0007	0.0082 ± 0.0014	0.0877 ± 0.0070	0.1129 ± 0.0096
		D 7	0.0160 ± 0.0009	0.0168 ± 0.0015	0.0979 ± 0.0003	0.1598 ± 0.0558
Al/VIN/5%EG/SBA-15	5 °C	D 0	0.0000 ± 0.0000	0.0000 ± 0.0000	0.0000 ± 0.0000	0.0000 ± 0.0000
		D 1	0.0012 ± 0.0002	0.0015 ± 0.0002	0.0018 ± 0.0002	0.0340 ± 0.0017
		D 3	0.0023 ± 0.0005	0.0025 ± 0.0007	0.0114 ± 0.0043	0.0483 ± 0.0050
		D 7	0.0038 ± 0.0002	0.0043 ± 0.0019	0.0216 ± 0.0035	0.0626 ± 0.0019
	25 °C	D 0	0.0000 ± 0.0000	0.0000 ± 0.0000	0.0000 ± 0.0000	0.0000 ± 0.0000
		D 1	0.0028 ± 0.0002	0.0017 ± 0.0010	0.0284 ± 0.0066	0.0411 ± 0.0052
		D 3	0.0035 ± 0.0012	0.0028 ± 0.0012	0.0430 ± 0.0267	0.0539 ± 0.0175
		D 7	0.0067 ± 0.0028	0.0035 ± 0.0007	0.0684 ± 0.0334	0.0987 ± 0.0166

product. The authors found that the migrated amount of α-tocopherol was delayed for 3.4 days in comparison to α-tocopherol, suggesting possible food applications of the active film studied. Another study reports that only 27% of thymol was released from SBA-15 after 24 h and that the carrier promotes the release of the active compound up to 31 days, reaching 69% of the release (Gámez et al., 2020).

Apart from the kinetic release of active compounds, the developments in the field of nanoencapsulation of natural bioactive compounds for food packaging systems are constantly growing (Beltrán & Valdés, 2021), owing to the ability of nanocarriers in protecting active compounds from degradation due to oxidation, light, high temperatures (Pascuta & Vodnar, 2022), preserving their activity, and enhancing their bioavailability (Munteanu & Vasile, 2021). In this regard, Li et al. (2021) studied the encapsulation of eugenol in nanocarriers as gelatin nanofibers aimed at food packaging applications, observing an increase of eugenol scavenging properties towards DPPH radical compared to that exerted by eugenol. Furthermore, Jia et al. (2020) studied eugenol-loaded nanoparticles (sodium caseinate and gum arabic) cross-linked by tannic acid observing that the complex exhibited improved antioxidant effects than EG. Nevertheless, the same authors stated that the used carriers needed cross-linking strategies to improve carrier delivery mechanisms, and then the AO activity of the complex. Nowadays, in Europe, the use of nanocarriers for food packaging applications, is regulated by EU 10/2011 which approves the use of carbon black, titanium nitride and silica nanoparticles (Gulin-Sarfraz et al., 2022). Among the latter, SBA-15 plays a key role in terms of ease of complexation and enhanced active molecule bioavailability. In this regard, Guntero et al. (2018) reported that the encapsulation of bis-eugenol in SBA-15 mesoporous silica nanoparticles enhanced the antioxidant activity of the molecule compared to that exerted by eugenol. Similarly, MoranteZarcero et al. (2022) demonstrated that MSNs enhanced the bioavailability of quercetin and naringenin as their antioxidant activity was found higher than that of non-encapsulated samples. These studies, together with the favourable features of SBA-15 such as biocompatibility and easy surface functionalization, encourage and support MSN application (Gámez et al., 2020).

3.3. Hydroxyl free radicals' generator

Antioxidant assays such as DPPH, ABTS and ORAC assays are indirect methods that require active compound extraction (Pyrzynska & Pękal, 2013), thus failing to provide antioxidant activity of the specific material. To verify the antioxidant activity of the existing coatings, a direct analysis of Al/VIN/5%EG and Al/VIN/5%EG /SBA-15 was applied to the coated film using an innovative technique relating the in situ vapour-phase generation of hydroxyl radicals and their determination with and without eugenol. The results are shown in Fig. 3 warranting further consideration regarding potential applications of the active coatings.

Significant difference of the Al/VIN/5%EG and Al/VIN/5%EG/SBA-15 coatings from the Al/VIN was observed (Dunnett's test, $p < 0.0001$), while no significant statistical difference was found between the two materials (one-way Anova, Tukey's multiple comparison test). This analysis yields noteworthy outcomes as Al/VIN/5%EG and Al/VIN/5%EG/SBA-15 scavenge more than 50% hydroxyl free radicals, since the hydroxylation percentage was equal to 43% and 46%, respectively. These results show that EG traps the free radicals and it doesn't need to be released or in contact with them acting (Wrona et al., 2017; Outjedi et al., 2019; Vera et al., 2018; Song et al., 2020).

4. Conclusions

Food oxidation is of great concern due to the huge amount of food wasted and terrestrial sources lost every year. This study demonstrates the antioxidant activity of aluminium flexible foils coated with a vinyl resin containing EG or eugenol loaded in SBA-15 MSNs.

As expected, the AO activity depends on time and temperature of exposure regarding the active materials. SBA-15 has proved to be a useful carrier in obtaining a slow release kinetic of eugenol, concurrently maintaining an adequate antioxidant activity of the material. Furthermore, the present study suggests that the two coatings are particularly suitable for the preservation and shelf-life extension of fatty foods.

Interestingly, two modes of action are highlighted herein in association with the designed materials. The first one is related to the activity of eugenol released into food/food simulants owing to the extraction properties of food/food simulants while the second one involves the feature of eugenol to scavenge the free radicals present in the packaging headspace without requiring direct contact with food/food simulants.

Considering that the potential application of food packaging materials requires their application in authentic food systems and their safety for human health, future research should focus on both testing its effectiveness on real food and on studying global and specific migration (according to the EU Regulation 10/2011) to assess the suitability of materials for food contact.

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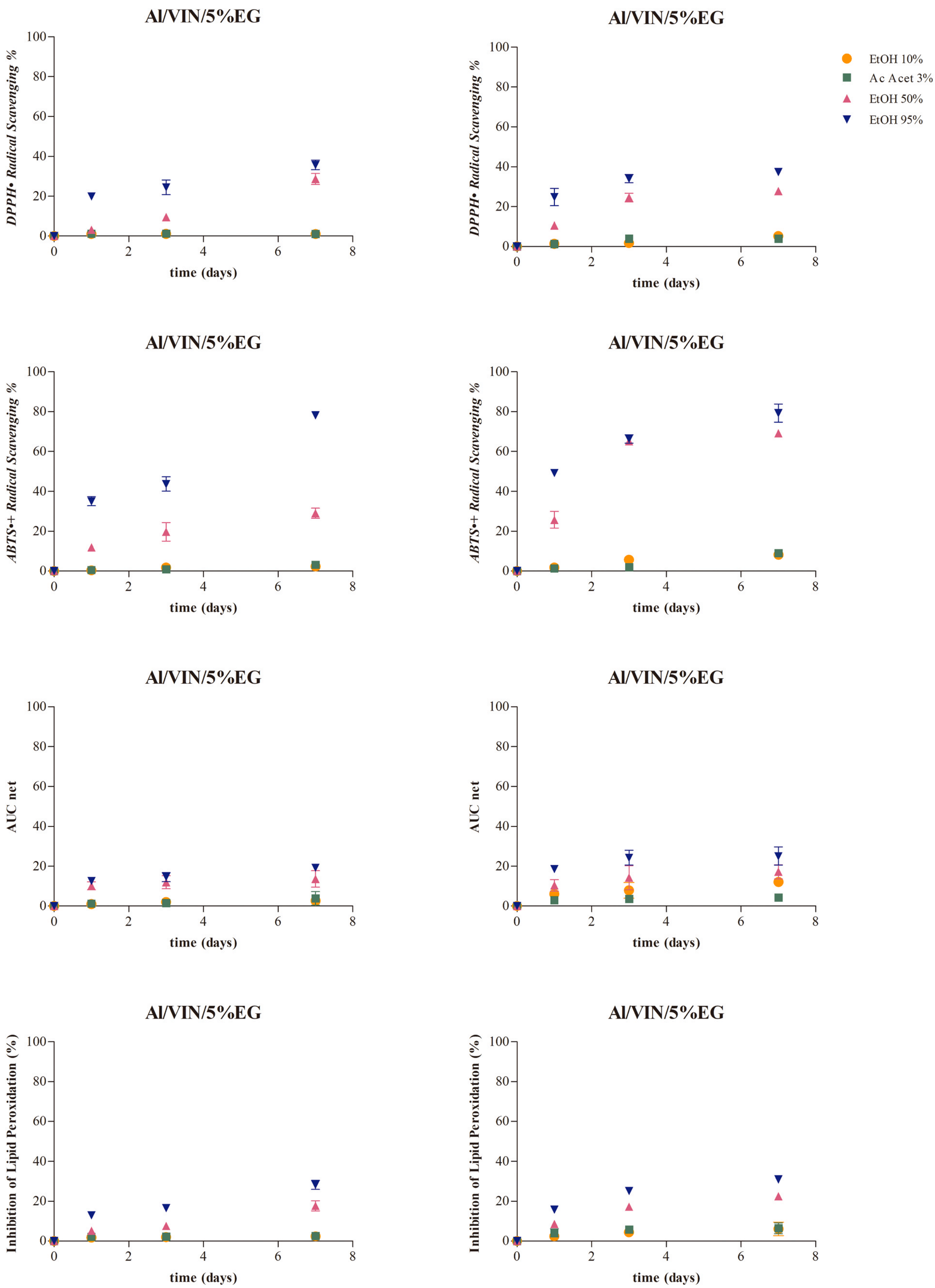

Fig. 1. Al/VIN/5%EG DPPH and ABTS radical scavenging activity. DPPH• and ABTS•+ scavenging activity (%), AUC_{net} value and inhibition of lipid peroxidation (%) of Al/VIN/5%EG after exposure to the food simulants for 0, 1, 3 and 7 days, at 5 °C (A) and 25 °C (B). The bars represent the standard error (n = 3).

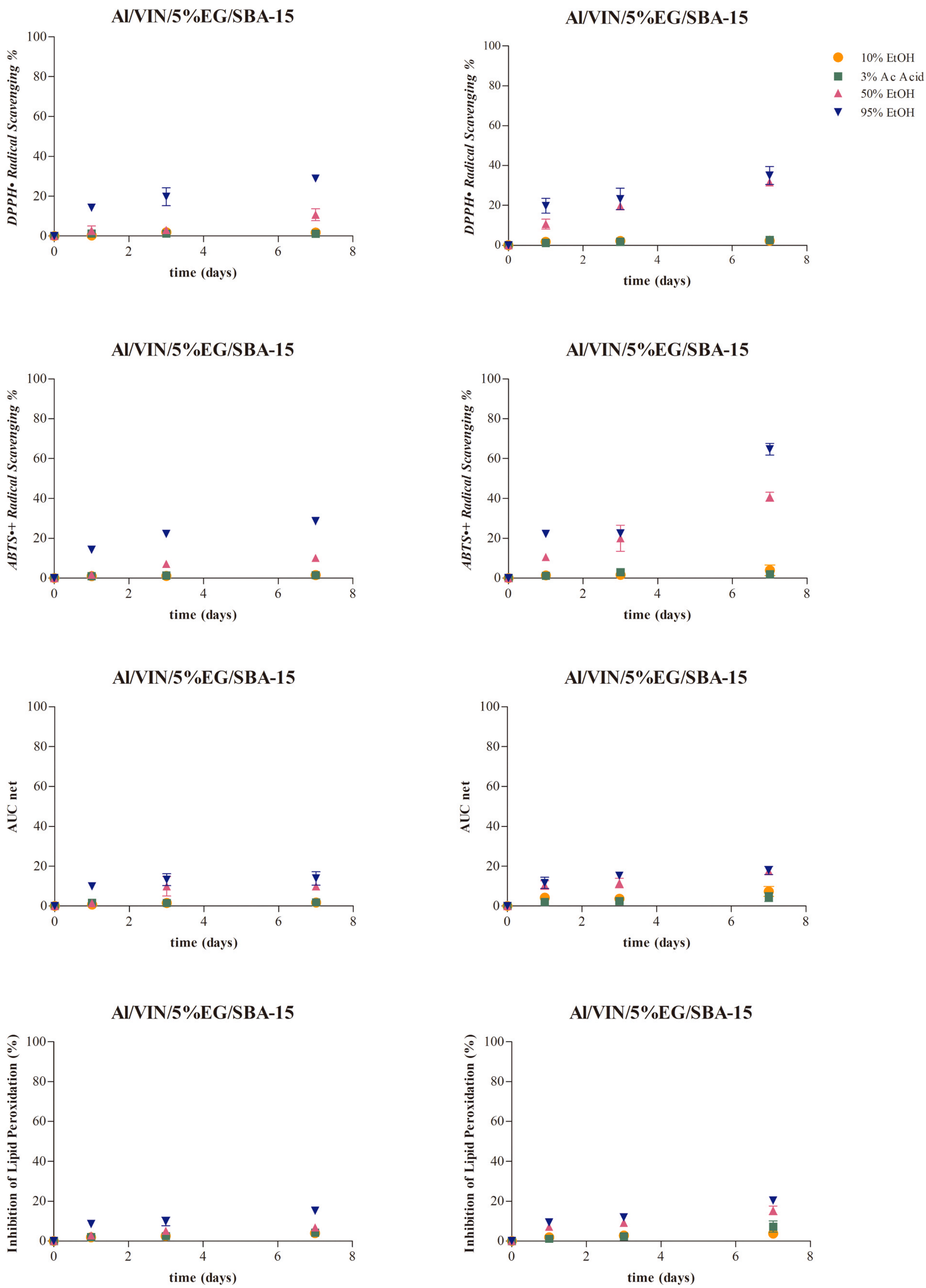

Fig. 2. Al/VIN/5%EG/SBA-15 DPPH and ABTS radical scavenging activity. DPPH$^{\bullet}$ and ABTS$^{\bullet+}$ scavenging activity (%), AUC$_{net}$ value and inhibition of lipid peroxidation (%) of Al/VIN/5%EG/SBA-15 after exposure to the food simulants for 0, 1, 3 and 7 days, at 5 °C (A) and 25 °C (B). The bars represent the standard error (n = 3).

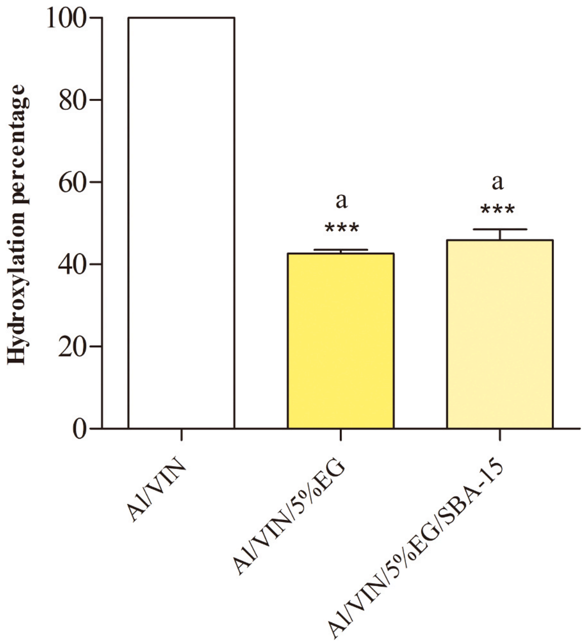

Fig. 3. Al/VIN/5%EG and Al/VIN/5%EG /SBA-15 Hydroxylation percentage. Hydroxylation (%) after 24 h (the Al/VIN neat coating is regarded as the 100% reference); the bars represent the standard deviation. Significant difference of the Al/VIN/5%EG and Al/VIN/5%EG/SBA-15 coatings from the Al/VIN was determined with one-way Anova Dunnett's test (***$p < 0.0001$). Letters indicate the significant differences among the two active coatings for $p < 0.05$ (one-way ANOVA, Tukey's multiple comparison test).

CRediT authorship contribution statement

Cristina Nerín, Margherita Lavorgna, Marina Isidori: Conceptualization, Supervision, Writing – review & editing. **Elena Orlo, Magdalena Wrona, Chiara Russo, Mariamelia Stanzione, Roberta Nugnes**: Methodology, Investigation, Data curation, Writing – original draft preparation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.fpsl.2023.101145.

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