Removal of bisphenol A in canned liquid food by enzyme-based nanocomposites

By: Natalia Tapia-Orozco, Fanny Meléndez-Saavedra, Mario Figueroa, Miquel Gimeno, and Roeb García-Arrazola

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Abstract:

Laccase from *Trametes versicolor* was immobilized on TiO_2 nanoparticles; the nanocomposites obtained were used for the removal of bisphenol A (BPA) in a liquid food matrix. To achieve a high enzymatic stability over a wide pH range and at temperatures above 50 °C, the nanocomposite structures were prepared by both physical adsorption and covalent linking of the enzyme onto the nanometric support. All the nanocomposite structures retained 40% of their enzymatic activity after 60 days of storage. Proof-of-concept experiments in aqueous media using the nanocomposites resulted on a > 60% BPA removal after 48 h and showed that BPA was depleted within 5 days. The nanocomposites were tested in canned liquid food samples; the removal reached 93.3% within 24 h using the physically adsorbed laccase. For the covalently linked enzyme, maximum BPA removal was 91.3%. The formation of BPA dimers and trimers was observed in all the assays. Food samples with sugar and protein contents above 3 and 4 mg mL^{-1} showed an inhibitory effect on the enzymatic activity.

Keywords: Bisphenol A removal | Laccase | Food matrix | Nanobiocomposites

Article:

Introduction

Research on the effective removal of emerging contaminants has increased in the last decade due to human health concerns and increasingly evident environmental issues. Among them, bisphenol A, 2,2-bis(4-hydroxyphenyl) propane (BPA) is a known endocrine disrupting chemical (EDC) that mimics the estrogen action binding to α and β estrogen receptors (ER), thus regulating the target gene expression. Accordingly, some reports have associated BPA exposure to neurobehavioral disorders, gonad alterations, metabolic abnormalities, diabetes, and breast cancer (Giulivo et al. 2016). Nonetheless, BPA is widely used to produce epoxy and phenolic

resins, polyacrylates, polycarbonates, and the interior coatings of food and beverages cans (Hirano et al. 2000; Cabana et al. 2007a). Several reports have demonstrated the migration of BPA from plastic and cans into the food matrices (Fasano et al. 2012; Cunha and Fernandes 2013; Mansilha et al. 2013; Sungur et al. 2014; Errico et al. 2014; Česen et al. 2016). Efforts for BPA removal are mainly focused on wastewater treatment through biological processes using fungi, aerobic, or anaerobic bacteria, and based on the pH, temperature, and oxygen levels in the medium (Chai et al. 2005; Zhang et al. 2013). In addition, the removal of EDCs has been studied via nanotechnological approaches, including doped TiO_2 (Sacco et al. 2015), graphene oxide-supported TiO_2 (Linley et al. 2014), a TiO_2 nanobelt (Liang et al. 2013), and other nanoparticles (Suyana et al. 2017). The FDA approves the use of food-grade titanium dioxide (> 100 nm) as a common additive that is not to exceed 1% of the food weight (Food and Drug Administration 2005).

The immobilization of active enzymes on nanoscale support materials, such as SiO_2 and TiO_2, has been recently proposed as a viable alternative to whole-cell culture processes because of their ability to degrade several low-molecular-weight xenobiotic compounds. The advantages of these nanostructured supports are: high enzyme loading capability, mass transfer resistance, and chemical and mechanical stability (Ahmed and Husain 2012). Furthermore, the immobilization of enzymes enhances the substrate selectivity, allows for mild operation conditions and reusability, and inhibits side-reactions (Mateo et al. 2007; Hanefeld et al. 2009; Carvalho 2011).

The immobilization of laccases on TiO_2 nanoparticles for BPA removal has been reported in aqueous model systems in a wide pH range (Hou et al. 2014a, b, c). BPA removal in food matrices, such as canned tea beverages, has been achieved via riboflavin photosensitization (Ha et al. 2009). However, there are no further reports on BPA removal in food matrices. Moreover, the effect of other components on the enzymatic activity has not been investigated.

In this work, the complete removal of BPA in canned liquid food samples using laccase from *Trametes versicolor* immobilized on TiO_2 nanocomposites is demonstrated. In addition, the effect of the food matrix on the nanocomposite activity is evaluated.

Materials and methods

Laccase from *Trametes versicolor* (E.C. 1.10.3.2) was purchased from Sigma-Aldrich (USA). Enzymatic activity was evaluated with 50 μL of enzyme in phosphate buffer pH 5.0 (100 mM) which were added to 2.9 mL of a 9.1 mM 2,2′-azino-bis(3-ethylbenzothiazoline-6-sulphonic acid) (ABTS, Sigma-Aldrich, USA) pH 5.0 solution. Then, a Genesys 10S UV–Vis spectrophotometer (Thermo Scientific) was used to analyse the mixture absorbance at 405 nm (ε_{405} = 36.8 M^{-1} cm^{1}) for 5 min at 25° C. One enzyme unit (U) corresponded to the amount of enzyme needed to produce 1 μmol of oxidized ABTS per min. The activity of the laccase solution (100 μg mL^{-1}) used in this work was 3.1 × 10^{-2} U L^{-1}. TiO_2 (21 nm) Degussa P25 TiO_2 (Aeroxide©, Sigma-Aldrich, USA) was employed as the nanocomposite (NC) support. 3-aminopropyl triethoxysilane (APTES) 10% (v/v) and glutaraldehyde 25% (v/v) were purchased from Sigma-Aldrich (USA). All solvents and reagents used for the NC characterization, proof of concept (PoC), and total BPA removal assays were of analytical grade. LC–MS solvents were employed for the extraction and chromatographic analysis. The BPA stock solution (10 mg

mL^{-1}) was prepared in methanol LC–MS Ultra (CHROMASOLV®, Sigma-Aldrich). All the glass material employed for the assays was treated before use at 120 °C for 3 h to eliminate organic residues.

Immobilization of laccase

Physical adsorption

A suspension of TiO_2 nanoparticles (10 mg mL^{-1}) in the laccase solution was incubated for 60 h at 4 °C under slight agitation. The resulting NCs were then subjected to centrifugation cycles at 6000 rpm for 10 min, replacing the supernatant each time with Milli-Q water. Cycles were halted when the enzymatic activity in the supernatant was null. The obtained NCs (T-Lac) were stored in the dark at 4 °C.

Covalent immobilization

A modified version of the methodology reported by Galliker et al. (2010) was performed. Briefly, a suspension of TiO_2/ethanol (0.5 g mL^{-1}) was prepared and sonicated for 15 min. An APTES/ethanol (10%) solution was prepared and purged with nitrogen for 15 min. The APTES solution (530 µL) was added dropwise to the TiO_2/ethanol suspension, and the reaction was carried out at 65 °C under an inert nitrogen atmosphere for 24 h. Nanoparticles were recovered by 10-min centrifugation cycles at 6000 rpm, and then resuspended in Milli-Q water, dried at 55 °C, and stored in a dark and dry environment at 4 °C. The modified TiO_2 nanoparticles were incubated with a 4% glutaraldehyde solution prepared in Sørensen buffer for 12 h at room temperature. The nanoparticles were then recovered and incubated in 5 mL of the laccase solution (100 µg mL^{-1}) for 60 h at 4 °C with slight agitation to obtain the covalently bonded NCs (TAG-Lac). TA-Lac NCs, without glutaraldehyde, were obtained from 50 mg of the modified nanoparticles directly incubated in 5 mL of the laccase solution (100 µg mL^{-1}) under slight agitation for 60 h at 4 °C. Recovery of both NCs proceeded by centrifugation cycles at 6000 rpm for 10 min and resuspension in Milli-Q water until the laccase activity in the supernatant was null. NCs were stored in a dark and dry environment at 4 °C.

Activity of NCs with immobilized laccase

A homogenized NC suspension (500 µL) was added to a reaction cell with ABTS buffer (500 µL) under slight agitation. NCs were then filtered using an MF Millipore MCE membrane (0.22 µm) and the filtrate was transferred to a 1 × 1 cm quartz cell for oxidation kinetic analysis. Laccase activity was determined by monitoring the oxidation rate of ABTS to $ABTS^+$ for 5 min at 405 nm (ε_{405nm} = 3.6 × 104 M^{-1} cm^{-1}).

Characterization of the NCs with immobilized laccase

Effect of temperature

NCs (50 mg) suspended in 5 mL of potassium phosphate buffer (0.1 M) were incubated in a water bath at 4, 21, 50, and 80 °C for 1 h. Assays were performed in triplicate. The enzymatic activity was measured as described in Sect. 2.2.

Effect of pH

Citrate 0.1 M (pH 3.0), phosphate 0.1 M (pH 7.0), and carbonate 0.1 M (pH 10.0) buffers were prepared. NCs (50 mg) were suspended in 5 mL of each buffer and incubated at 4 °C for 24 h. The enzymatic activity was determined as described in Sect. 2.2.

Shelf life

NCs were stored in sterile tubes in darkness at 4 °C. Enzymatic activities were monitored in the supernatant and NCs as previously described.

Total BPA removal assays

Proof of concept (PoC)

Experimental units consisted of 5 mL of sterile deionized water with an initial BPA concentration of 0.15 mg mL^{-1}. Next, 50 mg of NCs (T-Lac, TA-Lac, or TAG-Lac) were added to each unit under sterile conditions. The control test was prepared by adding 1 mL of a laccase solution and diluting to a 5 mL total volume. All experimental units were incubated at 21 °C and pH 7.0, where NCs showed the highest laccase activity. The assay was carried out by triplicate. Sampling was conducted at 48 and 120 h for the enzymatic activity measurement and BPA quantification.

BPA removal from a food matrix

Endogenous total BPA concentration was determined in a commercial tin canned peach nectar. Total BPA removal was assayed in 5 mL of the peach nectar with a known initial BPA concentration of 0.15 mg mL^{-1}. To each experimental unit, 50 mg of NCs were added and incubated at 21 °C. Sampling was performed every 6 and 24 h for laccase activity measurement and BPA quantification. The matrix effect on the enzyme activity was evaluated using six beverage dilutions between 0.04 and 0.75 $mL_{beverage}$ mL^{-1}. Total protein content was estimated by the Lowry method using bovine serum albumin as a standard (Waterborg 2002). Total reducing sugars were analysed by the dinitrosalicylic acid reagent modified method (Miller 1959).

Extraction of BPA

BPA extraction from the PoC samples was performed by addition of 5 mL of methanol (LC–MS grade) to each experimental unit. The sample was then vortexed for 1 min, sonicated for 10 min, and centrifuged (3000 rpm) for 5 min to separate the NCs. The supernatant (2 mL) was transferred to a chromatographic vial for total BPA quantification. BPA from food samples was

obtained by liquid–liquid extraction with dichloromethane (1:1) and the solvent from the combined organic fractions was evaporated under reduced pressure.

Detection and quantification of total BPA

Chromatographic analysis was performed in an ultraperformance liquid chromatography–mass spectrometer (UPLC–MS) Acquity Class (Waters, USA) equipped with a quaternary pump, sample manager, column oven, and photodiode array detector (PDA λ 190–500 nm) coupled with an SQD2 single-quadrupole mass spectrometer with an electrospray ion source (ESI). Instrument control, data acquisition, and processing were performed with the MassLynx software version 4.1. Samples were dissolved in methanol (spectrophotometric grade) and analyses were conducted using a BEH C18 column (2.1 × 100 mm, 1.7 μm, Waters) placed in a thermostat at 40 °C with a 0.1% formic acid aqueous solution (A) and methanol (B) mobile phase with a flow rate of 0.4 mL min^{-1}, and 5 μL of injection volume. Elution gradient was 0–2 min, 20% of B; 2–2.5 min, 50% of B; 2.5–4 min, 90% of B; 4–4.5 min, 99% of B. Line B flow was kept at 99% from 4.5 to 10 min, and then decreased to 50% from 10 to 12 min. The column was equilibrated with 50% of B for 2 min prior to injection. MS measurements were conducted in the negative mode (ESI-) with cone and capillary voltages of 42.0 V and 3.5 kV, respectively. The source temperature was set to 150 °C, the desolvation flow to 450 L h^{-1}, and nitrogen was used as collision gas. All sample extracts were filtered before injection with WWPTFE membrane filters (Acrodisc® MS 0.2 μm, 13 mm). The standard curve was obtained based on the chromatographic responses of BPA solutions with concentrations from 0.001 to 0.12 mg mL^{-1} using a linear regression program (R^2 = 0.9971).

Results

Design of Nanocomposites (NCs)

The enzymatic activity of the three different NCs is shown in Fig. 1 (T-Lac, TA-Lac, and TAG-Lac). At pH 7.0, the adsorbed protein (T-Lac) displayed the highest activity. In contrast, TAG-Lac showed the lowest enzymatic activity, with no detection at pH 3.0 and 10.0 (Fig. 1a).

As seen in Fig. 1b, the activity of T-Lac was significantly different ($p < 0.05$) at each temperature showing the following trend 50 °C > 21 °C > 4 °C > 80 °C. For the covalent strategy, TA-Lac showed the highest activity ($p < 0.05$) at 21 °C. Interestingly, both strategies also displayed laccase activities at 4 and 80 °C.

TAG-Lac had the lowest enzymatic response, which might indicate that glutaraldehyde immobilization had a negative impact on the laccase catalytic activity.

Experimental evidence confirms that T-Lac and TA-Lac had low laccase activity at 80 °C and alkaline pH. Notably, all the NCs displayed enzymatic activity after 60 days of storage at 4 °C. The TA-Lac showed a constant enzyme activity in the first 25 days and maintained 50% of the activity after 80 days. The physically adsorbed laccase NCs activity decreased from day 10 until no residual activity was found after 100 days. Finally, the NCs with glutaraldehyde lost 90% of laccase activity after 60 days.

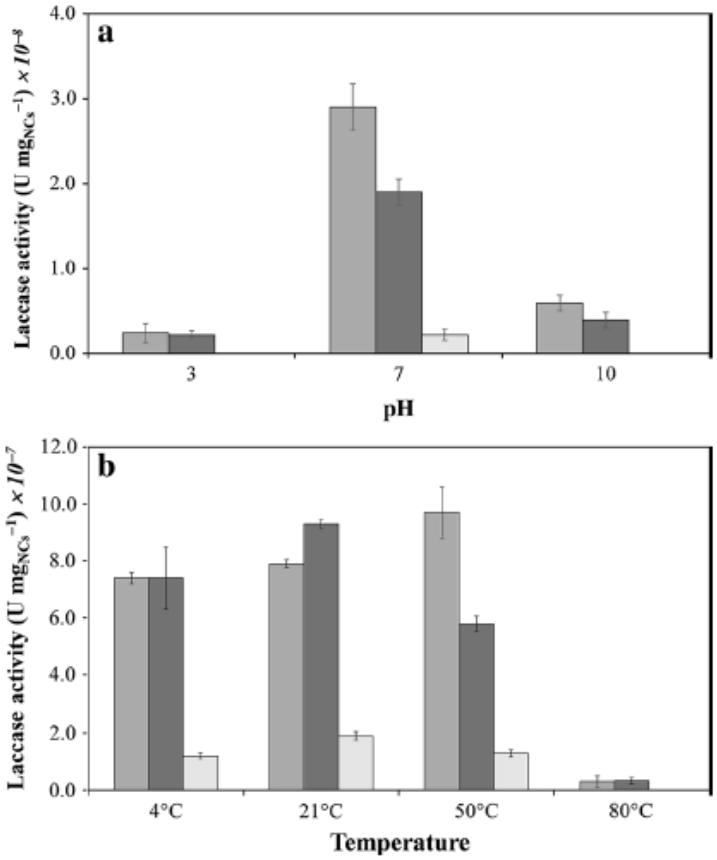

Figure 1. Laccase activity as function of pH (**a**) and temperature (**b**) for T-Lac (filled square); TA-Lac (filled square); and TAG-Lac (filled square)

Removal of BPA

The BPA removal capacity of NCs was evaluated with deionized water as a model matrix (PoC) at pH 7.0 and 21 °C. These conditions were selected based on previous results from the NC characterization. The BPA retention time in the LC-MS analysis was 6.71 min (*m/z* 227 [M-H]−). As seen in Fig. 2, BPA removal reached 60% within 48 h with all NCs and was below the chromatographic detection limit after 120 h of incubation with T-Lac and TAG-Lac.

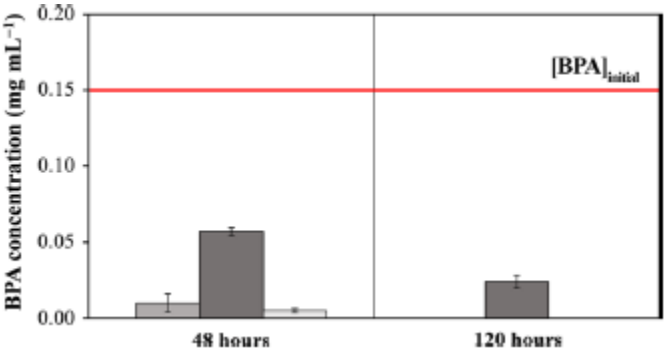

Figure 2. Residual BPA after PoC assays at 21 °C and pH 7.0 for T-Lac (filled square); TA-Lac (filled square); and TAG-Lac (filled square)

BPA removal in food matrix

The effect of protein and sugar content in the canned peach nectar on the NC efficiencies on BPA removal was observed above 3 and 4 mg mL^{-1}, respectively (Fig. 3). In addition, the immobilized laccase was very sensitive to pH changes in the food matrix, with an important loss of activity in a 3.2–3.9 pH range.

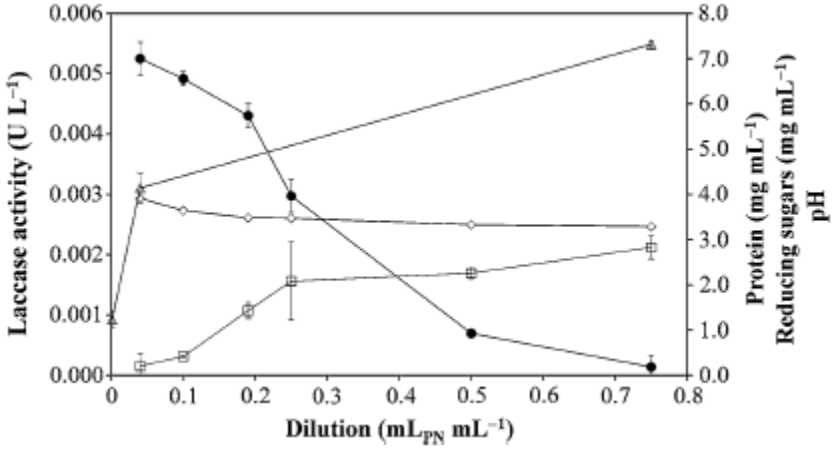

Figure 3. Laccase activity (filled circle) to protein content (open square), reducing sugars concentration (open triangle), and pH (open diamond) relationships in peach nectar

Accordingly, enzymatic inhibition caused by proteins and sugars was avoided by diluting to 0.25 mL mL^{-1} (Fig. 4). Statistically ($p < 0.05$), the T-Lac sample had the highest BPA removal (93.3% in 24 h). The covalently bound laccase NCs reached 91.3% (TA-Lac) and 66.0% (TAG-Lac) BPA removal in 24 h. Finally, the control assay (non-support laccase) showed a BPA removal over 80% after 3 h; however, an increase in residual BPA concentration was found after 24 h.

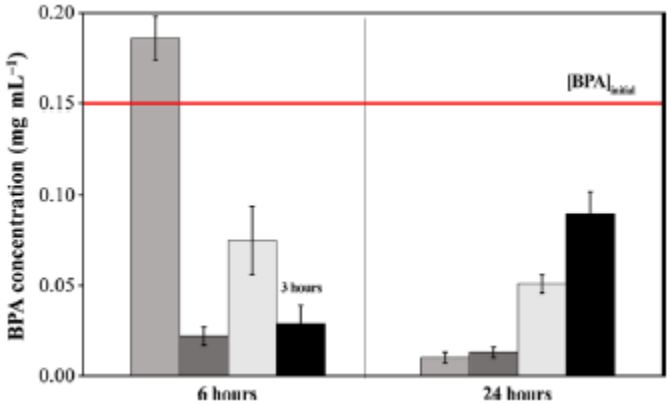

Figure 4. Concentration of residual BPA in peach nectar (0.25 mL mL^{-1}) for T-Lac (filled square); TA-Lac (filled square); and TAG-Lac (filled square) and control (filled square)

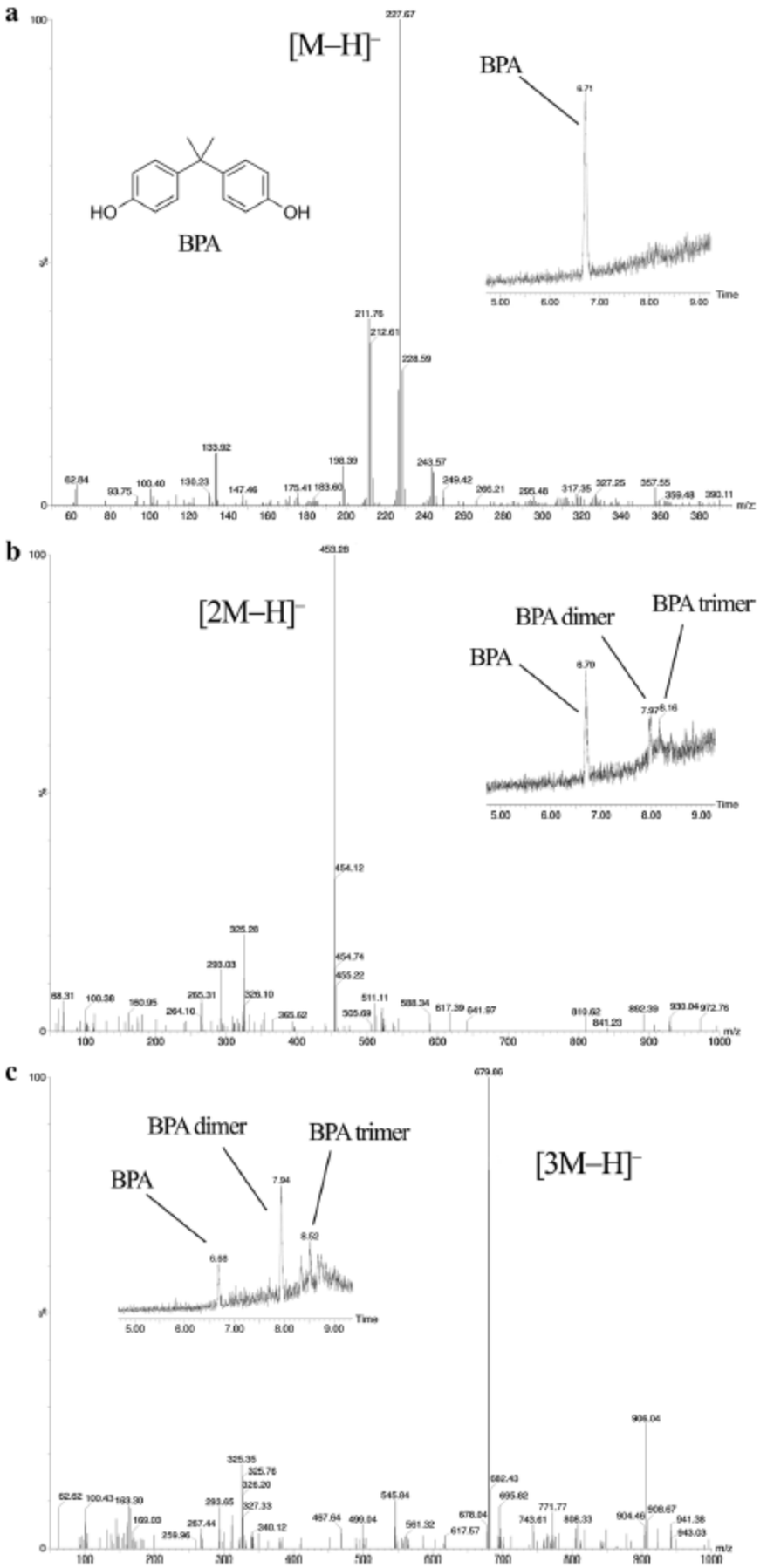

Figure 5. ESI-MS spectra of BPA (*m/z* 227 [M-H]$^-$) (A); BPA dimer (*m/z* 453 [2 M-H]$^-$) with TA-Lac at 6 h in food matrix assay (B), and BPA trimer (*m/z* 679 [3 M-H]$^-$) in control at 24 h in PoC assay (C). Insert: UPLC-MS chromatograms showing the retention times of BPA and its oligomers

BPA-derived products

The results of the MS analyses based on the most abundant ion showed no detection of BPA degradation metabolites. Nevertheless, the assays in the PoC and in the food matrix presented two peaks with retention times of 7.9 and 8.37 min, both with a molecular weight of *m/z* 453 [2 M-H]$^{-}$, which corresponds to BPA dimers as previously reported (Cabana et al. 2007b; Galliker et al. 2010). In addition, the experiments performed in aqueous media with all the NCs strategies showed peaks with *m/z* 679 [3 M-H]$^{-}$, which can be assigned to BPA trimers (Fig. 5).

In addition to the formation of BPA dimers and trimers, the food matrix control experiments with non-supported laccase showed the formation of BPA oligomers, (detected peak with *m/z* 785 [oligomer-H]−) (Fukuda et al. 2004; Galliker et al. 2010).

Discussion

Three of the temperatures used for this study were selected according to important food industrial processes: refrigeration temperature at 4 °C, an average shelf temperature of 21 °C, and the maximum pasteurization temperature at 80 °C. In addition, the temperature reported for maximum laccase activity is 50 °C (Han et al. 2005). The results indicate that the immobilization strategies may protect the active enzymatic structure at temperatures above 50 °C. The T-Lac and TA-Lac samples also showed remarkable activity under refrigeration conditions (4 °C). Furthermore, both NCs showed that enzymatic activity occurred at alkaline pH, which could lead to wider food applications (e.g., egg products). It is worth noting that no enzymatic activity was detected at 80 °C for non-supported laccase assays.

The absence of laccase activity in the TGA-Lac NCs at alkaline pH could be ascribed to the lack of glutaraldehyde-active monomers, i.e., the protein was not linked to the modified TiO_2 (Migneault et al. 2004); in addition, it may be due to impaired enzymes binding or to a gradual enzyme release (Walt and Agayn 1994). It has been reported that enzyme load and activity are affected by extensive crosslinking, which might lead to a distortion of the protein structure (Chen et al. 2013). A strongly acidic medium can enhance the affinity of laccase (Ip = 4.6) for anionic-like substrates (Jolivalt et al. 2005). On the other hand, media with pH above 4.6 would negatively charge the enzyme, thus improving its affinity for cationic substrates. The pKa for BPA has been reported between 9.6 and 10.2 (Hou et al. 2014b); therefore, the laccase-BPA linkage could be favoured in the 4.7–9.5 pH range.

Media conditions such as pH, ionic strength, concentration, and/or temperature are reported to strongly influence enzyme inactivation during the immobilization processes due to restrictions for the substrates to access the active site when the enzyme is attached in different random orientations (Galliker et al. 2010; Barbosa et al. 2012). Arroyo (1998) attributed this loss of activity to electrostatic, stearic, and diffusional effects. Other authors have reported that immobilization using glutaraldehyde as a cross-linker depends on the concentration of the monomers, leading to a high rigidity, increased dimer synthesis, and enhanced reactivity in certain moieties (Betancor et al. 2006). Different authors have found glutaraldehyde, despite being widely used for enzyme crosslinking via lysine amino groups not involved in the active site; the enzymatic activity can still be affected by the complete modification of the amino

groups or by formation of glutaraldehyde dimers, leading to support surface hydrophobicity (Barbosa et al. 2012; Migneault et al. 2004).

In addition, the vast majority of liquid canned foods have acidic pH and are normally processed at high temperatures, leading to BPA leakage from the inner coating (Sungur et al. 2014; Errico et al. 2014; Česen et al. 2016). Therefore, the nano-architecture developed in this work for enzyme-mediated BPA removal in both acidic and alkaline conditions, as well as at high temperatures, is promising.

The results indicate that BPA was successfully removed to below the chromatographic detection limit by T-Lac and TAG-Lac. Our findings agree with previously reported results. Galliker et al. (2010) developed a system based on laccase-modified silica nanoparticles functionalized with APTES and glutaraldehyde for BPA removal in McIlvaine buffer (0.1 M phosphate/0.05 M citric acid; pH 5). However, the authors observed a loss of specific catalytic activity of the enzyme due to partial inactivation or restricted accessibility to the active site. In addition, Hou et al. (2014b) employed TiO_2 nanoparticles with laccase to build a hybrid membrane reactor and achieved BPA degradation above 80% in simulated harsh industrial wastewater. These authors observed that the catalytic performance of the hybrid system was higher compared to the free form over a wide pH range. The reported BPA removal studies particularly rely on ideal aqueous systems and its application in wastewater treatment systems. However, food intake is the main route of human exposure to emerging contaminants, and specifically to BPA (Ballesteros-Gómez et al. 2009). Consequently, one of the objectives of the present study was to investigate the NCs performance in a real food sample. To this end, commercial tin canned peach nectar was doped with a BPA initial concentration of 0.15 mg mL^{-1} to evaluate the NCs removal capacity. The doped peach nectar, which was diluted to evaluate the enzyme inhibition by proteins and sugars, was subjected to treatment with the laccase-based NCs. The results showed effective removal of BPA to an acceptable range according to the Codex Alimentarius Commission "Pesticides Residues in Foods" (1993) that has established a range of 50–120% recovery for analyte concentrations < 1 μg kg^{-1}/μg L^{-1}.

In the food matrix assays, the NCs prepared by the adsorption strategy had the highest BPA removal after 24 h, followed by TA-Lac and TAG-Lac. The control assay (nonsupport laccase) showed an increase in residual BPA concentration after 24 h, which might be due to adsorption/ desorption or dimer formation mechanisms in the active site of the enzyme (Escalona et al. 2014).

Formation of BPA oligomers (dimers and trimers) was confirmed in the PoC as well as in the food matrix assays. The detected laccase-mediated oxidative oligomerization of BPA may be related to a decrease in estrogenic activity, because the estrogen receptor cannot bind these BPA derivatives with higher molecular weights than that of the EDC (Fukuda et al. 2004; Arboleda et al. 2013).

Conclusions

BPA removal from food matrices was successfully achieved using three NC architectures, T-Lac, TA-Lac, and TAG-Lac, which were obtained through physical adsorption or covalent laccase-

TiO_2 immobilization. The NCs maintained enzymatic activity in acidic, neutral, and alkaline pH values, as well as in a wide range of temperatures. For all the immobilization strategies, the activity remained even after 60 days of storage. The results showed that BPA was completely removed by the NCs in a model system (PoC) within 120 h and more than 90% was removed in a liquid food matrix (peach nectar) within 24 h. Formation of BPA oligomers (dimers and trimers) was confirmed in PoC as well as in the food matrix assays. It is worth noting that the effect of protein and sugar content in the food matrix on NC efficiency was circumvented when concentrations were, respectively, below 3 and 4 mg mL^{-1}. Further work is in progress to better understand the inhibitory effect of proteins and sugars on NCs and to improve the design of novel and robust NCs for BPA removal in a wide range of commercial food preparations.

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