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Use of Agri-Food Residues for Oil Structuring and Functionalization

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The residues from agri-food industry often represent an environmental burden, despite the fact that they are still rich in several intracellular compounds, which can be efficiently valorized if adequately recovered. This work addresses the use of High Pressure Homogenization (HPH) processing as an efficient comminution process to mechanically disrupt the plant cells and release the high-added value intracellular components into vegetable oils for their structuring and functionalization.
The vegetable matrices, consisting of tomato peels, or spent coffee grounds, were suspended in water, pre-milled and screened at 600 µm. Subsequently, the vegetable suspensions were processed from 1 to 5 times by HPH, at 100 MPa. Centrifugation (5000×g for 30 min) was used to separate the different fractions (oil phase, aqueous phase, and insoluble fibers). Vegetable oils were added to the dispersion before the HPH treatment or to the insoluble residues after centrifugation.
The results indicate that HPH processing causes the complete disruption of the vegetable cells in suspension and the release of the intracellular material. The resulting vegetable cell debris was exploited as an oil structuring agent, through the formation of a water-based capillary network into the continuous oil phase. The developed structuring capabilities of vegetable oils make possible to replace other undesired ingredients, such as palm oil, in food product formulation. Moreover, the lipophilic bioactive compounds contained in the vegetable cells were released in the oil fraction, becoming more readily bioaccessible.

1. Introduction

Residues from agri-food industry, including both by-products and wastes, often represent an environmental burden, either regarding the impact of their use in low-added value products (i.e. animal feed, compost) or their disposal. However, they represent an opportunity to contribute to the economic and social benefit, because still rich in valuable compounds, which can be efficiently valorized if adequately recovered (Mirabella et al., 2014).
Many active ingredients, such as proteins, polyphenols, lipids, polysaccharides, and fibers are tightly locked inside the plant cells, making their recovery with high yields a significant technological challenge (Ravindran and Jaiswal, 2016). The main limit to the exploitation of active ingredients from agri-food residues is, in fact, represented by the difficulties associated with their mass transfer through the cell membranes. While polysaccharides and fibers are mostly contained between the primary and secondary cell walls, proteins, antioxidants, and lipids are mainly contained in storage bodies, i.e. vacuoles, or lipid vescicles within the cell cytoplasm. Therefore, in the first case, the damage of the primary cell wall layer is required, whereas in the second case, more intense or selective processing is needed, including physical disruption or permeabilization of inner membranes (Donsì et al., 2010, 2013).
Conventional extraction methods include hydrodistillation or classic solvent extraction. However, organic solvents are very often potentially toxic, and their use may also cause serious environmental problems. Also, they still generate a waste material (mainly water insoluble fibers from cell walls debris), which needs to be disposed of (Ravindran and Jaiswal, 2016).
More natural (with minimal heat or chemical treatment) and sustainable approaches should be addressed to minimize the waste streams and also exploit the contribution of the water insoluble part of the waste material,

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achieving the “total use” or “zero waste” concepts. In particular, selective permeabilization of cell membranes or enhanced cell disruption could enable at the same time the better control of the purity of the extracts and the increase of process yields (Donsì et al., 2010).
Wet milling of plant materials using HPH is based on mechanical disruption of cell walls and membranes, to unlock with high yield the intracellular compounds (Donsì et al., 2009a). In an HPH process, a liquid dispersion of the plant material is pressurized between 50 and 300 MPa in a continuous system and is pumped to a specifically designed micrometric disruption chamber, where lamination occurs to atmospheric pressure. Owing to the micrometric dimensions of the disruption chamber, the cell suspension is suddenly accelerated and subjected to intense fluid-mechanical stresses (shear, elongation, turbulence and cavitation), which cause the physical disruption of cell wall and membranes (Donsì et al., 2009a, 2009b, 2013).
The aim of this work is to investigate the potential contribution of HPH processing of suspensions of two types of food wastes, tomato peels from tomato processing, and spent coffee grounds, to unlocking the functionality of these waste materials, and pursue their total use as novel oil-structuring agents.

2. Materials and Methods

2.1 Materials

The tomato peels were collected from a local factory for tomato processing (FDP s.r.l., Fisciano, Italy), ground with a laboratory blender to a size comprised between 1 and 2 mm, and stored at -18 °C until further use. The spent coffee grounds (SCG) from Arabic beans were collected from a local bar in Pagani (Italy), and stored at -18 °C until further use. Peanut oil was bought from a local supermarket (Sagra, Italy). The chemicals for lycopene analysis were from Sigma-Aldrich (Milan, Italy).

2.2 Particle micronization

Tomato peels or SCG were micronized by high pressure homogenization (HPH). Suspensions of tomato peels or SCG were prepared in bidistilled water, with a dilution ratio of 1 to 5 (w/w). The suspensions were finely dispersed in water by high shear mixing with a T-25 Ultra Turrax device (IKA, Germany), for 5 min at 20,000 rpm. Subsequently, the resulting suspension was sieved with 600 μm mesh as a precautionary procedure to prevent blockage of the homogenization valve. The suspension was then processed by HPH, using an orifice valve assembly (orifice diameter of 200 μm) for 5 passes at 100 MPa. The particle size of the suspensions was characterized by light scattering (Malvern Mastersizer 2000, Malvern Instruments Ltd., UK), evaluating the characteristic diameters $D_{0.1}$, $D_{0.5}$ and $D_{0.9}$, corresponding to 10 %, 50 % and 90 % of the cumulative particle size distribution, as well as by optical microscopy (Nikon Eclipse TE2000-S).

2.3 Preparation of Pickering emulsions

Pickering emulsions were prepared by HPH. Suspensions of tomato peels (10 %wt) and peanut oil (10 %wt) in bidistilled water, were homogenized to form a coarse emulsion by high shear mixing with a T-25 Ultra Turrax device (IKA, Germany), for 5 min at 20,000 rpm. Subsequently, the emulsion was processed by HPH, using the same conditions as for particle micronization. The particle size of the emulsions was characterized by light scattering (Malvern Mastersizer 2000, Malvern Instruments Ltd., UK).

2.4 Lycopene analsysis

The Pickering emulsions were broken by centrifugation (5000 × g for 30 min), the addition of acetone (1/1 w/w) and further centrifugation. Lycopene was quantified by spectrophotometric analysis at 472 nm, against a calibration curve using a lycopene standard in acetone. The purity of the extracts was also evaluated by reversed-phase high-performance liquid chromatography using isocratic elution and UV detection at 472 nm (Waters, Belgium). A carotenoid C30 reversed-phase column (250 × 4.6 ID, 3 μm) from YMC Corporation (Waters, Belgium) was used with MeOH/isopropyl alcohol/THF (30:30:35) containing 250 ppm BHT and 0.05% TEA as mobile phase. The flow rate was 1 mL/min, column temperature was 35 °C and the injection volume 20 μL., according to the method described by Cucu et al. (2012).

2.5 Preparation of capillary suspensions

The solid particles were separated from the suspension as pellets by 2-stage centrifugation (5000 × g for 30 min). Subsequently, the water was completely dried in oven for 72 hr at 80 °C. Finally, the particles were dispersed in peanut oil (25 %wt) using the high shear mixer. The capillary suspensions, where the peanut oil was the continuous phase and the micronized tomato peels or SCG were the dispersed solid phase, were obtained by adding bidistilled water as a secondary fluid, which formed capillary bridges among the solid particles. The secondary fluid was gradually added at different ratios with the primary fluid.

2.6 Rheological characterization of capillary suspensions

The apparent yield strength of capillary suspensions, at different weight ratios S_{sec} of secondary fluid (water) to continuous phase (oil) was measured using a rotational rheometer (AR 2000, TA Instruments, US) with a conical concentric cylinder geometry (ID 15 mm, OD 28 mm, cone angle 2 °). For viscoelastic materials, the apparent yield strength is defined as the stress at which the sample begins to flow irreversibly. It was found by locating the intercept of a line that is drawn tangentially to the curve formed (stress vs. shear rate) in the case of pseudo plastic behavior, at the point where the curve slope does not significantly change as the shear rate increases. The shear rate ramping test was conducted at 20 °C, starting at 0.1 s^{-1} to 100 s^{-1} for 120 s.

3. Results

3.1 Particle micronization

The effect of HPH on the particle size distribution of both tomato peels and SCG is shown in Figure 1, in terms of percentile diameters as a function of the number of passes. Despite the different initial size distribution of the two matrices after high shear dispersion in water, a similar trend can be observed upon HPH processing, with a reduction in particle size, whose median value attains an asymptotic value after 5 passes. The inserts of Figure 1a also show that, while high shear dispersion is not able to break the plant cells, after 5 passes of HPH the cells are completely disrupted, releasing the intracellular content, and only cell debris can be found in the suspension. One of the main effects of HPH processing was to unlock the bioactive compounds contained in the plant cells, with a significant enhancement of the antioxidant activity of the suspension (+ 20 % for tomato peel suspensions and + 80 % for SCG suspensions, data not shown). The increase in antioxidant activity has already been observed for the microfluidization of aqueous suspensions of corn bran (Wang et al., 2014) or wheat bran (Wang et al., 2013), which has been attributed to the release of bioactive compounds into the aqueous medium, as well as to the increased bioaccessibility of antioxidant compounds still bound to the solid cell debris (surface antioxidant activity). The data herein reported refers only to the antioxidant activity of the compounds released in the aqueous phase.
The HPH micronization process significantly affected also the surface area of the particles, which increased of about 60 % for tomato peels and 50 % for SCG. The increase in surface area has profound implications on the capability to form either Pickering emulsions or capillary suspensions, as discussed in the following sections.

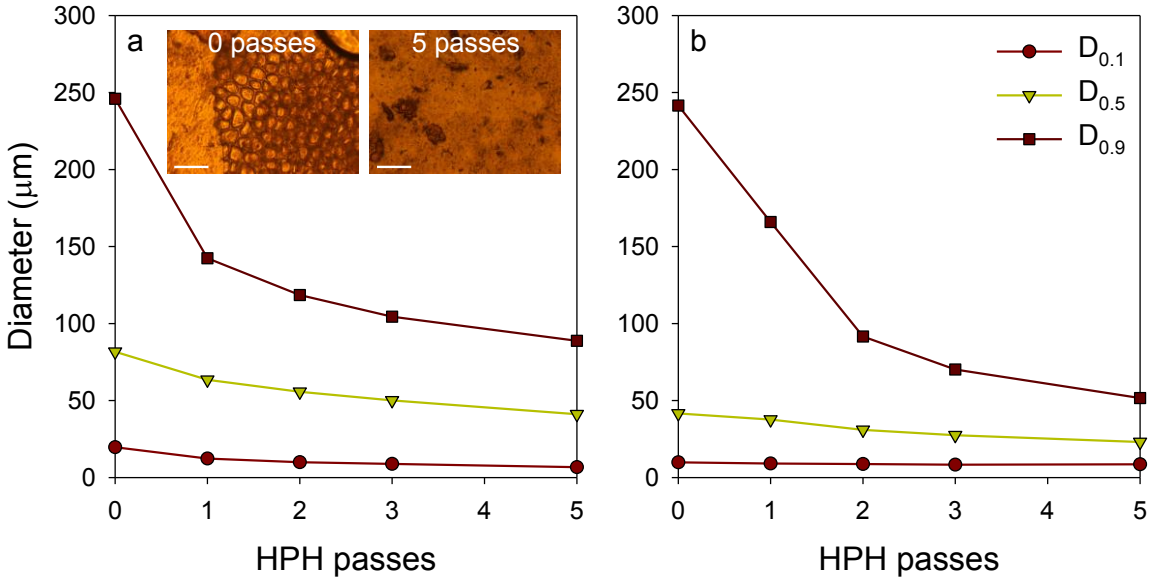

Figure 1: Effect of HPH processing on the micronization (reported as percentile diameters of the cumulative distribution) of tomato peels (a) or SCG suspensions (b) at 10 %wt in water. Inserts of Figure 1a show micrographs of tomato *peel suspensions before and after 5 passes of HPH treatment (scale bar = 100 µm).*

3.2 Pickering emulsions

Pickering emulsions were prepared using tomato peels. HPH processing of tomato peels, peanut oil and water caused the micronization of the plant cells and, concurrently, also the emulsification of the oil. The emulsion

droplets were stabilized by the micronized tomato peel particles adhering to the oil-water interface. The concept of food-grade Pickering emulsions stabilized by food-grade particles is not new, and its advances have been recently reviewed (Xiao et al., 2016). In general, the stabilization of emulsion droplets can be achieved not only by small molecular weight surfactants, or amphiphilic macromolecules but also through dispersed colloidal particles, with well-defined properties. In particular, the general principles for solid particles to function as Pickering emulsion stabilizers are: i) particles can wet both continuous and dispersed phase, ii) particles are substantially insoluble in both phases; iii) particle wettability is only partial, to gain sufficient interface absorption efficiency; iv) particle size is substantially smaller than the targeted emulsion droplet size (Xiao et al., 2016).

The tomato peels suspension exhibited insolubility in both oil and water (ii), and wettability by both phases (i), which as only partial (iii), as confirmed by contact angle measurements. Three-phase measurement of the contact angle of water droplets in oil deposited on a bed of micronized tomato peels showed, in fact, a mean value of contact angle of 72.6 ° ± 8.8 ° (data not shown). The mean droplet size of the obtained Pickering emulsion was of about 20 µm (data not shown), which is smaller than the mean value of micronized tomato peels (Figure 1a), suggesting that only the smaller fraction of tomato peels particles were involved in emulsion droplet stabilization, in compliance with principle iv. The fraction of tomato peels particles with larger sizes likely remained in suspension with the emulsion droplet, as confirmed by microscopic observations.

The process of fabrication of the Pickering emulsions had a remarkable effect on lycopene extraction, which was transferred to the oil phase, as shown in Figure 2. In particular, Figure 2b shows the reddish color of the oil phase after the emulsion was broken by centrifugation. The oil was analyzed to quantify the lycopene content, indicating an increase in lycopene extraction of about 20 % after 5 HPH passes with respect to the sample subjected only to high shear dispersion (HSH), as shown in Figure 2a. The extracted lycopene corresponded to about 10 % of the total lycopene content of the peels (9.3 mg/g_{peels}). Remarkably, HPLC chromatogram (insert of Figure 2a), in addition to showing the increased amount of lycopene recovered, also indicates that part of lycopene is converted from the trans isomer to the cis isomer, which is more readily absorbed in the gastrointestinal tract (Stahl and Sies, 1992).

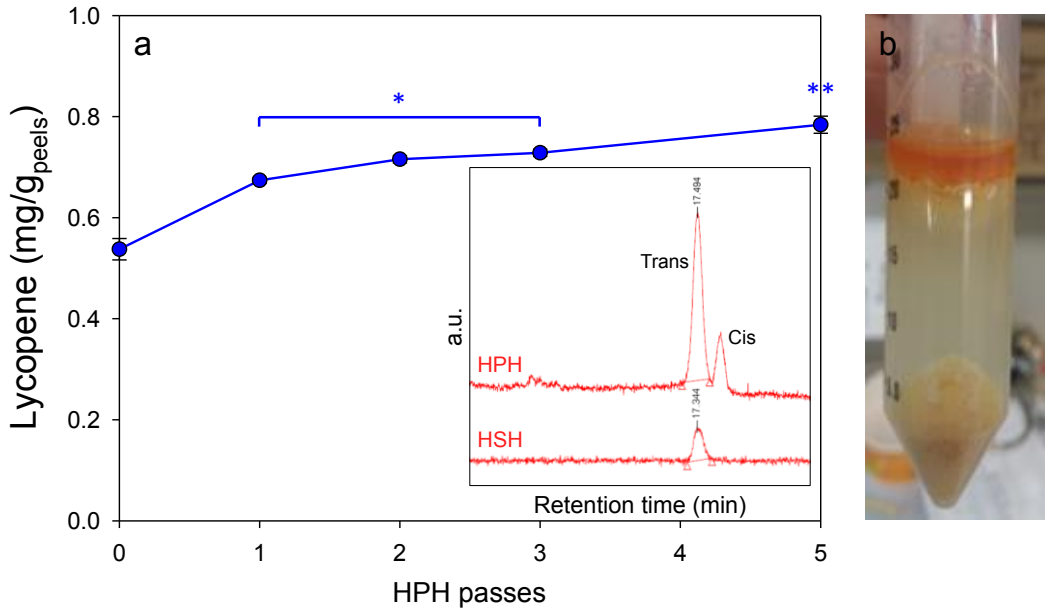

Figure 2: (a) Effect of HPH processing on the extraction of lycopene from tomato peels into the oil phase. The insert shows the chromatogram from HPLC analysis of the extracted carotenoids, which consist mainly of trans-lycopene in the case of high shear dispersion (HSH) and trans- and cis-lycopene in the case of HPH sample. (b) Appearance of the peanut oil after HPH processing and after the emulsion being broken by centrifugation.

3.3 Colloidal suspensions

Owing to their partial wettability by both the oil and the water phase, the tomato peels and the SCG were also exploited in the fabrication of colloidal suspensions, to act as oil structuring agents. The addition of a second immiscible liquid to the continuous phase of a suspension dramatically alters the rheological properties of the system, which can change from a fluid-like to a gel-like state (Koos et al., 2012).

The idea of exploiting capillary bridges to stabilize particle suspensions, as well as to tune the flow behavior of food suspensions is not new (Hoffmann et al., 2014). The addition even of a small fraction of an immiscible fluid to a particle suspension can lead to particle bridging and network formation. This effect has been reported to occur for secondary fluid wetting the particles better or worse than the bulk fluid (Hoffmann et al., 2014).

Tomato peels and the SCG were preliminary micronized by HPH in water suspension, and then dried and dispersed in the oil phase. Drying is not necessary from a technological point of view but was carried out to precisely control the amount of water present in the system. In fact, the addition of water causes the formation of capillary bridges among the solid particles, contributing to form a network structure, which significantly alters the rheological behavior of the oil.

This is particularly evident in Figure 3a, where the effect of water addition at a weight ratio with the oil S_{sec} of 0.46 clearly reveals the structuring capability on peanut oil. However, when particles with larger size are used, as in the case of those simply dispersed by high shear mixing (HSH), the structuring capability is only limited, and some oil can be seen to exudate from the network of water and particles. This phenomenology can be observed both for tomato peels and for SCG. In contrast, in the case of HPH-treated samples, a significantly firmer structured system can be observed, with the oil, which is kept well inside the network of water and particles. The firmer structure of HPH samples has been quantified by measurements of apparent yield stress as a function of the water addition parameter S_{sec} in the case of tomato peels. Figure 3b shows that the finer size of HPH-treated particles, with the associated higher surface area and larger number of particles present, is fundamental in obtaining a firmer structure, characterized by values of the apparent yield stress more than one order of magnitude larger than in the case of the system prepared with the particles treated by high shear mixing. A similar concept was previously discussed, in the study of the effect of glass beads of different sizes suspended in diisononyl phthalate, upon the addition of 0.60 % of water (Koos et al., 2012).

It can be speculated that the higher structuring capability demonstrated by HPH-treated particles derives not only from the higher surface area and number of particles available for establishing the capillary bridges but also from the activation, consequence of the high-intensity processing, of the macromolecules and fibers contained in the sample. However, this hypothesis requires further experimental verification.

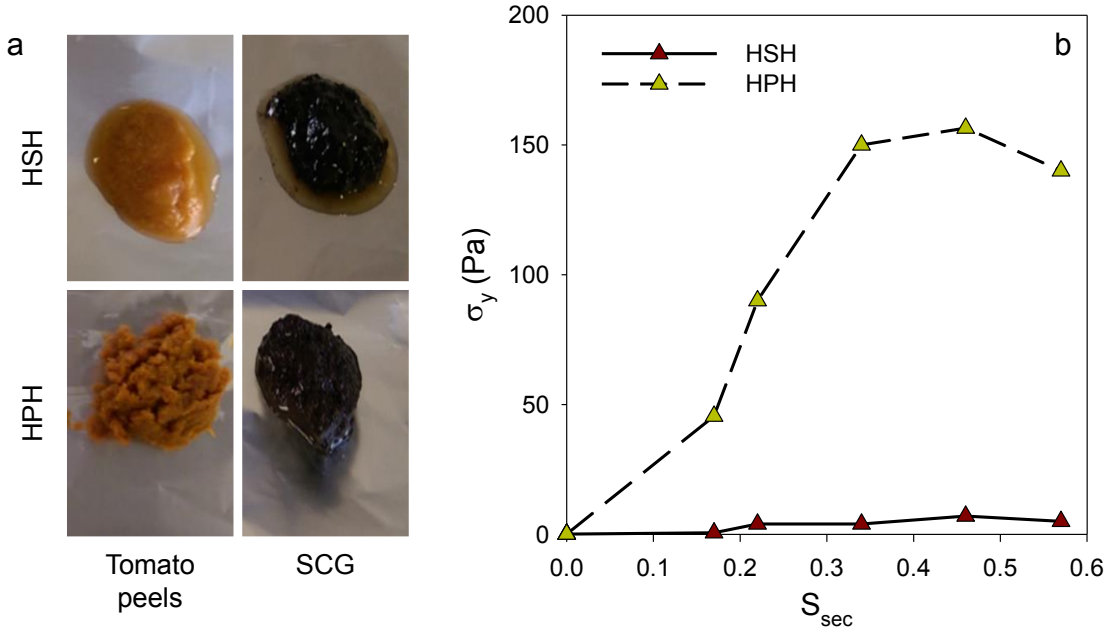

Figure 3: Capillary suspensions obtained by dispersing micronized tomato peels or SCG in peanut oil and adding different amounts of water as secondary fluid (S_{sec} = weight ratio of water to oil). (a) Appearance of capillary suspensions prepared with samples treated by high shear dispersion (HSH) or HPH (5 passes at 100

MPa), upon addition of water at S_{sec} =0.46. (b) Apparent yield stress of capillary suspensions prepared with tomato peels (processed by HSH or HPH) as a function of S_{sec}.

4. Conclusions

This work shows that the process of high pressure homogenization, through the complete unlocking of the functionality of agri-food residues and the fragmentation of the plant cells, can be exploited in different ways.
One possibility is the preparation of food-grade, natural oil-in-water Pickering emulsions, where the particles act as stabilizers at the oil-water interface, with the additional advantage of transferring part of lycopene into the oil phase, where it is more readily bioaccessible.
Another possibility is the use of the micronized plant material as an oil structuring agent, upon dispersion in an oil phase, and the addition of water as a secondary fluid to form capillary bridges among the particles. In this case, the size reduction achieved through the comminution process plays a fundamental role in controlling the rheological behavior of the system. The natural structuring of the oil might find several applications, especially in replacement of solid fats, such as palm oil, also taking advantage of the null caloric content of the structuring agents (primarily water and fibers).

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