

Extract from pomegranate waste as an alternative natural antioxidant in foods

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Oil oxidation is a free radical chain process leading to the deterioration of oil and lipid containing materials. In foods, these reactions can lead to rancidity, loss of nutritional value from the destruction of vitamins (A, D, and E), and essential fatty acids, and the possible formation of toxic compounds and colored products. In order to overcome this problem, synthetic antioxidants, such as butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), and ter-butylhydroquinone (TBHQ), have been used as food additives. However, recent reports revealed that these compounds may be implicated in many health risks (Schillacia, 2013). In view of these negative health effects, in the past decade a considerable interest has emerged for the use of antioxidants of natural origin. The use of natural antioxidants in the food industry is a common practice, the use of phenolics from agricultural and forestry byproducts being an excellent option that fulfills this objective. In addition, phenolics have been shown to act as inhibitors against foodborne pathogens and as functional components of enriched foods both to color the products and to supplement with biofunctional plant metabolites.

Pomegranate is one of the healthiest fruits worldwide with a considerable amount of various phenolic compounds. The processing of pomegranate fruit into juice produces enormous amounts of by products, such as peels and seeds, leading to environmental pollution. Peels and seeds constitute approximately 78 and 22% of pomegranate by products, respectively, and either are used as cattle feeds or directly disposed as wastes (Doymaz, 2012). However, pomegranate peels were found to contain higher amounts of phenolics than the edible fleshy parts and could be a good source for producing high-value antioxidants. Li *et al* (2005) have reported that pomegranate peels contain 249.4 mg/g phenolics compared to just 24.4 mg/g phenolics in the pulp. Several studies have been published to extract phenolics from pomegranate peels with various extraction methods. Recently, the aqueous conditions for extracting phenolic compounds from pomegranate peels have been optimized by Kaderides *et al* (2015). Numerous research works study the antioxidant effect of pomegranate peel extract in various food products, such as cooked chicken (Naveena *et al*, 2008), sunflower oil (Iqbal *et al*, 2008), ice cream (Cam *et al*, 2013), hazelnut paste (Kaderides *et al*, 2015), and beef meatballs (Turgul *et al*, 2016).

However, the effectiveness of polyphenols depends on preserving the stability, bioactivity, and bioavailability of the active ingredients (Fang & Bhandari, 2010). According to Cilek *et al* (82), there are unsaturated bonds in the molecular structure of polyphenols, which makes them susceptible to oxidants, light, heat, pH, water, and enzymatic activities. Munin and Edwards-Lévy (83) reported that the instability of phenolic compounds, during food processing, distribution or storage, or in the gastrointestinal tract (pH, enzymes, presence of other nutrients), limits the activity and the potential health benefits of polyphenols. Unfortunately, they oxidize very quickly, leading to the progressive appearance of a brown color and/or unwanted odors with a considerable loss in activity. In addition, many phenolic compounds show limited water solubility and have an unpleasant taste, which must be masked before their incorporation in foodstuffs or oral medicines. Therefore, the administration of phenolic compounds requires the formulation of a finished protecting product able to maintain the structural integrity of the polyphenol until the consumption or the administration, mask its taste, increase its water solubility and bioavailability, and convey it precisely towards a physiological target. Microencapsulation is one of the techniques that is used for enhancing the shelf life and stability of phenolics.

Kaderides and Goula (2017) encapsulated pomegranate peel phenolic extract by spray drying using a new encapsulating agent from orange juice by-products as wall material. Thus, two food wastes that are beneficial to health – the edible orange byproduct fiber and the antioxidant pomegranate peel extract – were combined into one multipurpose functional food.

In this study, a stability trial of the crude and the encapsulated with orange wastes extract incorporated into three types of food products for different storage times was carried out. Cake and smoothie samples were enriched with crude and encapsulated extract at a phenolics concentration of 5000 ppm (w/w) and both extracts were added to sunflower oil at two concentrations (500 and 1000 ppm). For the storage study, the smoothie and cake products were kept at 4 and 25°C, respectively. For the sunflower oil, due to the time-consuming nature of the testing of storage conditions at 40°C or lower, the simple accelerated method of using oven storage at 60°C was carried out. Samples were periodically withdrawn during the storage in order to measure peroxide value (PV), total phenolics content (TPC), antioxidant activity (AA), and color. In addition, HPLC analyses were used

for the determination of individual phenolic compounds in the samples. Finally, a 9-point scale acceptance test (1 for extremely dislike, 9 for extremely like) was used to determine the acceptability of enriched samples.

In the case of cakes, it was observed that a large amount of the phenolic compounds were degraded during baking even if they were encapsulated. However, encapsulation had a significant effect ($p < 0.05$) on the retention of phenolic compounds and their activities as compared to uncoated. As it can be seen, the incorporation of encapsulates not only improved the nutritional value (polyphenol content and antioxidant activity) of the products, it enhanced the storage stability of these properties as well. During the storage period, there was no loss in polyphenols, while the antioxidant activity of supplemented products in some cases slightly declined. A continuous increase in PV with the increase in storage period was observed for all the samples due to the formation of hydroperoxides, i.e. primary oxidation products. After a storage period, there was a tremendous rise in PV of control samples, followed by a decrease. Initially, the difference in peroxide content of control and enriched samples was not noticeable; it became significant ($p > 0.05$) just after heating up to 4-12 days. All the samples containing extract had lower values of PV than the control sample. The higher inhibition rate of crude extract may be attributed to the fact that in the crude extract the polyphenols are not protected and thus, are more susceptible to oxidation and further polymerisation to form oligomers with a higher antioxidant activity. However, the crude extract did not solubilise completely and over time it tended to precipitate, but still showed a significant antioxidant effect.

The results showed that the enriched products had acceptable sensorial qualities. Compared to the control sample, sensory scores of enriched products showed significant ($p < 0.05$) changes in color scores. Color became darker in enriched products, partly due to higher level of polyphenols present. Encapsulated extract addition caused a decrease in the scores for surface appearance, while addition of crude extract did not affect this attribute. Cakes shape became deformed with increased level of encapsulated powder, possibly due to the higher water absorptivity resulting in cakes hardness. The evaluators also reported mild residual taste in samples with encapsulates described as “milky”, probably because of high fiber content. It is important to note that the panelists haven't perceived the aroma associated with phenolic extract and evaluated the taste as being similar for both samples. Thus, the process of encapsulating pomegranate peel polyphenols and their incorporation in different products described in this study represent a promising way for functional food development due to antioxidant content and storage stability provided by encapsulation.

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