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Effect of olive mill wastewater phenolic extract, whey protein isolate and xanthan gum on the behaviour of olive O/W emulsions using response surface methodology

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ABSTRACT

Spray-dried polyphenols extracted from olive mill wastewater (OMW) were used to formulate 20% olive oil-in-water (O/W) emulsions stabilised with whey protein isolate (WPI) and xanthan gum at pH 7. The effects of olive biophenol extract (0.9–4.4 mM), whey protein isolate (0.13–0.5%) and xanthan gum (0.06–0.2%) on the physical stability (creaming index), viscosity, emulsion droplet size and distribution, primary and secondary oxidation products were assessed over accelerated storage of emulsions. Response surface methodology (RSM) was applied for experimental design using three-factor central composite design (CCD) with 3 central points.

The effects of OMW phenolics, WPI and xanthan gum were statistically significant on emulsion creaming rate, viscosity, PV, TBARS and cloudiness. Second-order polynomial models were obtained for predicting these responses, resulting in good performances especially for the first two responses. High coefficient of determination (R^2) values ranging from 0.847 to 0.973 were obtained for creaming and viscosity, acceptable R^2 values were obtained for lipid oxidation parameters (peroxide value and TBARS) and cloudiness value, while non-significant results were obtained for mean droplet size. The performance of the model was particularly good for creaming rate and viscosity. It has been highlighted that the interactions between OMW phenolic extract and the ingredients studied should be considered for the formulation of olive O/W emulsions. This research could be useful for the formulation of functional food products based on O/W emulsions, as well as understanding the physico-chemical interactions among olive biophenols, whey proteins and xanthan gum.

1. Introduction

A wide range of foods are emulsions, e.g. mayonnaise, salad dressings, sauces, etc., and other food products include emulsions as an ingredient, e.g. yoghurts, ice creams and whipped products (Traynor, Burke, Frias, Gaston, & Barry-Ryan, 2013). Food emulsions are kinetically unstable systems as the lipid and water phases tend to separate over storage (McClements, 2004a; Mirhosseini, Tan, Hamid, Yusof, & Chern, 2009).

Many stabilisers are usually added to food emulsions to improve their stability and lead to a longer shelf life, or improve the appearance, rheology and other factors (Mirhosseini, Tan, Taherian, & Boo, 2009; Sun, Gunasekaran, & Richards, 2007). Polysaccharides, including xanthan gum, have been widely applied in the food industry, due to their characteristics related to its visco-elastic properties and its chemical properties, in particular the water solubility and pH stability (Sun et al., 2007). Proteins are also used in oil-in-water (O/W) emulsions to facilitate their formation, improve their stability and provide specific physicochemical properties. Milk proteins, i.e. whey protein isolate and caseinate, and soy proteins have been reported (McClements, 2004b). The ability of food manufacturers to formulate emulsion-based products with desirable and reproducible characteristics depends on

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knowledge of the relationship between the emulsion properties and matrix composition as well as microstructure (Mirhosseini, Tan, Hamid, et al., 2009). For this reason, it is of great interest to study the interaction between stabilisers and other compounds added to give specific functional properties in O/W emulsions.

Olive oil is one of the most appreciated vegetable fats, and is of paramount importance in the Mediterranean diet, which has been linked to human health benefits (López-Miranda et al., 2010). Olive oil has been described as a natural functional food, due to its composition and presence of valuable phytochemicals, including phenolic compounds, squalene and α-tocopherol (Stark & Madar, 2002). There is a great difference between virgin olive oils and "olive oil", as this latter product is defined by law as the mixture of refined olive oil with a non-defined percentage of virgin olive oil. This in turns signifies that the majority of olive oil on the market is not virgin, i.e. undergo a refining process, and usually these oils are used for emulsion production. At the same time, huge amounts of olive biophenols are lost during the virgin olive oil extraction process because these compounds are highly hydrophilic and their partitioning in oil is limited. These compounds are therefore highly concentrated into the olive mill wastewater (OMW).

A possible approach to increase the phenolic content of olive oils and other refined vegetable oils, and therefore to increase the nutritional profile of oils and high fat foods, could be the addition of olive phenolic compounds recovered from by-products of olive oil extraction, i.e. olive mill wastewater. OMW leads to important environmental issues in olive oil producing countries because of its high pollution risks due to its high chemical oxygen demand. OMW also contains high concentrations of phenolic compounds derivatives of secoiridoids (oleuropein, ligstroside) and verbascoside (e.g. hydroxytyrosol, tyrosol, caffeic acid), vanillic acid, luteolin-7-glucoside, etc. (De Marco, Savarese, Paduano, & Sacchi, 2007). Alternatives for its disposal and innovative ways for the application of the extracted phenolic compounds in food products are therefore important research questions (Garcia-Castello, Cassano, Criscuoli, Conidi, & Drioli, 2010; Schieber, Stintzing, & Carle, 2001).

Response surface methodology (RSM) is usefully applied as an effective tool for the optimization of a process when the independent variables can exert a combined effect on the desired response (Koocheki, Taherian, Razavi, & Bostan, 2009). RSM has been previously applied by other researchers to study the behaviour of food emulsions and the dependence of emulsion stability on their ingredients (Gharibzahedi, Mousavi, Hamedi, & Ghasemlou, 2012; Mirhosseini, Tan, Hamid, et al., 2009; Mirhosseini, Tan, Taherian, et al., 2009; Traynor et al., 2013). Among the advantages of its application, RSM allows the design of a comprehensive model describing the characteristics of a system, by minimizing the number of experiments required. Central Composite Design (CCD) is one of the most common forms of RSM applied to various food systems (Ahmed, Rico, Martin-Diana, & Barry-Ryan, 2011). This approach was therefore applied in the present research.

Whereas the characterisation of O/W emulsion behaviour is a widely researched topic, little is still known about olive O/W emulsions formulated with stabilisers like WPI and xanthan gum, with particular emphasis on the possible effects of olive biophenols. In this context, the use of these phenolic extracts for the development of a functional food is of great interest for the food industry and might help in the valorisation of olive by-products.

Therefore, the aim of the present paper was to evaluate the effect of phenolic compounds concentration on the stability of oil-in-water emulsion made by using refined olive oil, WPI and xanthan gum as stabilising agents. Emulsions were added with phenolics as powder extract (P-OMW) obtained from olive mill wastewater membrane filtration. The response surface methodology (RSM) was used to build statistical models able to describe both the physical behaviour and oxidation stability of emulsion.

2. Materials and methods

2.1. Olive oil sample, stabilisers and OMW extract

Freshly refined olive oil was donated by I.O.B.M. srl (Montesarchio, BN, Italy). Xanthan gum from *Xanthomonas campestris* was purchased from Sigma–Aldrich (Darmstadt, Germany). WPI was 97.5 wt% protein, and lactose content was less than 1 wt%. A phosphate buffer solution at pH 7.0 was prepared using monosodium phosphate and sodium hydroxide (SA, Darmstadt, Germany). The buffer was used to maintain constant pH, as this parameter can affect emulsion stability (Sørensen et al., 2008). All other chemicals were of analytical grade purity. Phenolic powder extract from OMW was donated by LABS (Department of Agricultural Sciences, University of Naples Federico II, Italy). P-OMW production process has been reported by Troise et al. (2014) and the emulsions formulated with these extracts were previously applied for other studies on O/W emulsions (Caporaso, Genovese, Burke, Barry-Ryan, & Sacchi, 2016). The composition of the three main phenolic compounds analysed by HPLC-UV-Vis was as follows: OHTy 32 ± 0.2 mg g^{-1}, Ty 1.9 ± 0.1 mg g^{-1}, verbascoside 2.8 ± 0.09 mg g^{-1} (Troise et al., 2014).

2.2. Experimental design

RSM was applied in the present experiment to study the effect of P-OMW, WPI and xanthan gum on olive O/W emulsion properties and stability over storage. The effect of three independent variables, i.e. P-OMW (0.01–4.4 mM, expressed as hydroxytyrosol equivalent), xanthan gum (0.06–0.25% w/w) and WPI (0.13–0.63% w/w) were studied in relation to the emulsions physical and oxidative stability. In particular, the creaming index, mean droplet size, turbidity, lipid hydroperoxide formation and TBARS were assessed over the storage period.

The experimental design was based on central composite design (CCD), with three replicates of the central point, and data was fitted with a second order polynomial equation. ANOVA and regression surface analysis were used to determine the statistical significance of the model factors and responses and to calculate a regression equation based on the experimental data. The mathematical model used to describe the variation in the responses used the following equation:

$$Y = \beta_0 + \Sigma\beta_i x_i + \Sigma\beta_{ii} x_i^2 + \Sigma\beta_{ij} x_i x_j + \varepsilon \quad (1)$$

where Y is the response value predicted by the model; β_0 is a offset value; β_i, β_{ii} and β_{ij} are the main (linear), quadratic and interaction regression coefficients, respectively (Neter & Wasserman, 1992).

The software uses a quadratic model to build response surfaces. The complete design consisted of 17 experimental points (runs) including 3 replicates of the central point. The concentrations of the P-OMW, xanthan gum and WPI that were used in the 17 runs for the RSM are reported in Table 1.

The range of concentrations of the hydrocolloids and OMW phenolics were chosen according to previous works (Di Mattia, Sacchetti, Mastrocola, & Pittia, 2009; Sun et al., 2007). In particular, the minimum and maximum concentration of OMW biophenols were chosen based on previous literature regarding the natural content of olive oil biophenols (Caporaso et al., 2015), and calculations were made to mimic similar amounts expressed as hydroxytyrosol equivalent (Caporaso et al., 2016).