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Optimization of a soft degumming process of crude rapeseed oil—Changes in its antioxidant capacity

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ABSTRACT

A modified soft degumming process of crude rapeseed oil for maximizing phospholipid removal and minimizing losses of antioxidants was proposed and optimized by response surface methodology. The effects of water volume, degumming time, and concentration ratio of sodium dodecyl sulfate to disodium ethylenediaminetetraacetate on the concentration of phospholipids and phenolics and antioxidant capacity of oils were evaluated. The soft degumming process removed phospholipids from the crude oil (94.9–98.7%) more effectively than industrial acid degumming (95.3%). Moreover, rapeseed oils revealed high phenolic content (20.0–22.1 mg sinapic acid (SA)/100 g) and antioxidant capacity, as determined by ferric-reducing antioxidant power (FRAP = 301–328 μmol Trolox equivalent (TE)/100 g), 2,2-diphenyl-1-picrylhydrazyl (DPPH = 528–739 μmol TE/100 g), and 2,2′-azinobis-3-ethylbenzothiazoline-6-sulfonic acid (ABTS = 1300–1505 μmol TE/100 g) methods.

The predicted optimum water volume (11.5 mL), time (19.7 min), and concentration ratio of sodium dodecyl sulfate to disodium ethylenediaminetetraacetate (=1) resulted in total phospholipids = 67 mg/kg, phenolics = 20.8 mg SA/100 g, FRAP = 313 μmol TE/100 g, DPPH = 617 μmol TE/100 g, and ABTS = 1346 μmol TE/100 g.

Replacement of industrial acid degumming by the proposed soft degumming can improve the stability of rapeseed oil with potent antioxidant capacity.

1. Introduction

Phospholipid (PL) molecules include a hydrophilic head group and hydrophobic fatty acid chains. It is known that PLs can improve the oxidative stability of vegetable oils, and they are synergists of phenolic antioxidants. Although these compounds exhibit therapeutic properties and can be applied to improve human health by lowering cholesterol level and treating neurological disorders, unfortunately, they have a negative effect on technological processes and the organoleptic properties of rapeseed oils (Choe and Min, 2009; Fine et al., 2016). Therefore, these compounds must be removed from the crude oil during the refining process.

Refining (degumming, neutralization, bleaching, and deodorization) of crude vegetable oils removes undesirable compounds (PLs, proteins, pigments, oxidation products, and free fatty acids) and the solvent that was used for the oil extraction, thus improving the oil quality and shelf life (Landucci et al., 2013). However, bioactive compounds such as phenolics, tocopherols, carotenoids, and phytosterols can be lost during the refining process. Therefore, the industrial conditions applied along the different steps of chemical refining (especially lower temperature and shorter time of deodorization, selection of alkaline agents and suitable bleaching earth during neutralization, and bleaching steps) and replacement of the conventional processes by alternative new technologies are key factors for the preservation of bioactive components in fully refined oils.

The first step of crude oil refining is degumming, which mainly consists of PL removal. Over the years, different degumming techniques have been developed: acid degumming; acid-basic degumming; and dry, membrane, enzymatic, and soft degumming (Choukri et al., 2001; Niazmand et al., 2011, 2015; Sampaio et al., 2015; Vaisali et al., 2015; Zufarov et al., 2008). The conventional degumming process, which includes both water degumming (to remove the hydratable PLs) and

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acid degumming by citric or phosphoric acid treatment (to remove the non-hydratable PLs), is widely applied in the oil industry. However, this technique does not provide maximum PL removal from oil rich in non-hydratable PLs. The water degumming process of crude extracted and pressed rapeseed oils decreases the phosphorus content by approximately 92% and 61%, respectively, whereas acid degumming using citric acid caused higher losses of phosphorus (98% and 89–80%) in the extracted and pressed rapeseed oils (Zufarov et al., 2008; Wei et al., 2015). Moreover, the quantity and type of PLs in the oil affect the efficiency of the chemical degumming process.

Furthermore, the industrial acid degumming process can lead to the activation of precursors of carcinogenic contaminants such as 3-chloropropane-1,2-diol esters (Ermacora and Hrncirik, 2014). Therefore, conventional degumming should be replaced by other processes that have many advantages such as higher efficiency, milder reaction conditions, ambient temperature operation, low energy consumption, reduction of contaminants, and retention of bioactive components.

Recently, enzymatic degumming using enzymes such as phospholipases A1, A2, B, and C and microbial enzymes to hydrolyze PLs has been developed for the reduction of phosphorus levels to 3.91–48.91 mg/kg in rapeseed oil and for oil yield improvement (Clausen, 2001; Jiang et al., 2011, 2014a; Liu et al., 2015; Sampaio et al., 2015; Wei et al., 2015; Yang et al., 2006; Ye et al., 2016). Phospholipase A1, which hydrolyzes PLs into lysophospholipids and free fatty acids, and phospholipase C, which produces diacylglyceride and phosphate ester acid after hydrolysis, are the most commonly used enzymes in the oil industry (Xie and Dunford, 2017). Enzymatic treatment using phospholipase A1 and phospholipase C effectively reduced the PL concentrations (6.49–7.52 and 8.75–12.14 mg/kg, respectively) in crude rapeseed oil in comparison with that in control crude oils (PLs = 252.05 and 690.44 mg/kg, respectively) (Jiang et al., 2014a; Ye et al., 2016). Somewhat higher concentrations of phosphorus (3.91–48.91 mg/kg) were revealed in rapeseed oils after degumming by using a novel microbial lipase (Lecitase® Ultra) and phospholipase A1 from *Fusarium oxysporum* (Lecitase® Novo) (Clausen, 2001; Yang et al., 2006). In addition, a higher phosphorus level (20.74 mg/kg) was determined in phospholipase A2-treated rapeseed oil within 6 h (Liu et al., 2015). However, the phosphorus content decreased to 5.7 and 4.5–4.9 mg/kg after enzymatic hydrolysis at time = 4 and 5 h with phospholipase B from *Pseudomonas fluorescens* BIT-18 and *Thermotoga lettingae*, respectively (Jiang et al., 2011; Wei et al., 2015). Although enzymatic degumming offers a biological, cleaner, and eco-friendly improvement of vegetable oil refining, industrial applications of enzymes for oil degumming are limited because of the high cost of enzymes, difficulties in their reuse and separation from the reaction medium, and the necessity for new devices.

The removal of PLs from rapeseed oils by membrane technology is a relatively new development. This type of degumming minimizes the number of steps, energy and chemical consumption, and losses of oil and bioactive compounds. After membrane degumming, the phosphorus concentration in rapeseed oils ranged between 0.3 and 319.6 mg/kg (Hafidi et al., 2005; Niazmand et al., 2011, 2015; Subramanian and Nakajima, 1997; Subramanian et al., 1999). The major problems in membrane separation are the poor flux in solvent-free conditions and the instability of membranes, which delay the application of this technique at an industrial scale. Therefore, conventional techniques of vegetable oils degumming should be modernized.

Choukri et al. (2001) proposed a new physicochemical process, so-called soft degumming, for PL elimination from crude vegetable oils by using a chelating agent, disodium ethylenediaminetetraacetate (EDTA) in the presence of an emulsifying agent. The effects of chelating and emulsifying agent concentrations, oil phase to aqueous phase ratio, temperature, and degumming time on the PL removal were evaluated. The soft degummed vegetable oils contained 0.0–9.0 mg phosphorus per kg of oil (Choukri et al., 2001).

In addition, monoethanolamine, diethanolamine, and triethanolamine were used as degumming agents for the elimination of non-hydratable PLs from crude rapeseed and sunflower oils (Zufarov et al., 2009). The concentration of phosphorus in rapeseed and sunflower oils significantly decreased (97.3–99.7% and 91.8–99.6%, respectively) after ethanolamine treatment.

Moreover, the influence of some degumming modifications on the concentrations of minerals, sterols, tocopherols, polyphenols, and soaps; oxidative stability; and color of rapeseed oils was studied (Hafidi et al., 2005; Niazmand et al., 2011, 2015; Jiang et al., 2011, 2014a; Sampaio et al., 2015; Wei et al., 2015; Subramanian et al., 1999; Ye et al., 2016; Zufarov et al., 2009).

However, to the best of our knowledge, there are no reports on the evaluation of the effect of soft degumming process on total phenolic content (TPC) and antioxidant capacity (AC) of rapeseed oils after treatment with EDTA.

The industrial acid degumming process of crude rapeseed oil causes significant losses of natural antioxidant compounds; thus, it seems worth to consider the modernization of this refining step for the production of rapeseed oil with high quality and potent antioxidant properties.

Therefore, this work focused on the optimization of the proposed soft degumming conditions for effective PL elimination from crude rapeseed oil with minimal loss of antioxidants. Moreover, for the first time, the AC of rapeseed oils after modified soft degumming and industrial acid degumming were compared and discussed. Response surface methodology (RSM) was applied as a useful statistical tool to predict the optimum experimental conditions for soft degumming and describe the relationships between the independent variables based on more responses with a reduced number of experimental trials. The effects of three independent variables, namely volume of water (V_{water}), degumming time (t), and concentration ratio of sodium dodecyl sulfate (SDS) to disodium EDTA, were studied. In addition, the effects of these three variable on the response variables, namely total PL concentration, TPC, and AC of soft degummed rapeseed oils, determined by using three modified analytical methods, ferric reducing antioxidant power (FRAP), 2,2-diphenyl-1-picrylhydrazyl (DPPH), and 2,2′-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid (ABTS), were estimated in this study.

2. Materials and methods

2.1. Reagents

All reagents were of analytical or HPLC grade. Sinapic acid (SA, 98%), 6-hydroxy-2,5,7,8-tetramethylchromane-2-carboxylic acid (Trolox, 97%, TE), ABTS diammonium salt (99%), DPPH radical, 2,4,6-tri(2-pyridyl)-s-triazine (TPTZ, 99%), ammonium metavanadate (99.8%), and ammonium molybdate (99.9%) were obtained from Sigma–Aldrich (Poznań, Poland). Iron(III) chloride hexahydrate, SDS (85%), disodium EDTA (99%), magnesium oxide, nitric acid (65%), Folin–Ciocalteu reagent, sodium carbonate anhydrous (99.8%), acetic acid (99%), sodium acetate, hydrochloric acid (30%), ethanol (99.8%), and methanol (99.8%) were purchased from POCH (Gliwice, Poland). Redistilled water was used for the preparation of solutions.

2.2. Samples

Pressed rapeseed oils [crude and degummed (after conventional acid degumming)] were kindly provided by a local vegetable oil factory. All rapeseed oils in the original packing (polypropylene containers) were stored at 4 °C in the dark until analysis.

2.3. Laboratory soft degumming process

Crude rapeseed oil sample was weighed (100 g) on a technical balance (RADWAG WTB 2000, Warsaw Poland), transferred into a beaker, and heated on a hot plate with magnetic stirring (IKA RH B2, Łódź, Poland) to 70 °C. Then 5, 10, and 15 mL of hot distilled water (above 90 °C) was added under stirring