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Ultrasound-assisted extraction of pomegranate seed oil – Kinetic modeling

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ABSTRACT

In this work, ultrasound-assisted extraction was employed to extract oil from pomegranate seeds. Seed particle size, extraction temperature, solvent/solid ratio, amplitude level, and pulse duration/pulse interval ratio were the factors investigated with respect to extraction yield using a central composite design. The optimum operating conditions were found to be: seed particle size, 0.2 mm; extraction temperature, 20 °C; solvent/solid ratio, 20/1; amplitude level, 60%; pulse duration/pulse interval ratio, 5/15. Under these optimized conditions, the predicted value for extraction yield was 59.8%. A second-order kinetic model was successfully developed for describing the mechanism of ultrasound extraction under different processing parameters.

1. Introduction

Pomegranate (*Punica granatum* L.) is one of the oldest known edible fruit that contains the highest concentration of total polyphenols in comparison with other fruits studied (Fazaeli et al., 2012). Pomegranates are rich in aril, the percentage of which ranges from 50% to 70% of total fruit and comprises of 78% juice and 22% seeds (Mohagheghi et al., 2011). According to Eikani et al. (2012), pomegranate seeds show average contents of about 37–143 g/kg of fruit. Oil content of seeds varies from 12% to 20% of the seed on a dry weight basis (Al-Maiman and Ahmad, 2002). Pomegranate seed oil consists of 65–80% conjugated fatty acids, the most important of which is 9-trans, 11-cis, 13-trans, octadecatrienoic acid, the so-called punicic acid (Abbasi et al., 2008a), and has the highest botanical concentration of a sex steroid (estrone) at 17 mg/kg dry seed (Abbasi et al., 2008b).

Pomegranate seed oil was reported to present biological properties (Eikani et al., 2012), such as antioxidant and eicosanoid enzyme inhibition properties (Qu et al., 2010), immune function and lipid metabolism (Yamasaki et al., 2006), estrogene content (Tong et al., 2006), skin photoaging inhibition effect (Park et al., 2010), lipoperoxidation and activity of antioxidant enzymes (Melo et al., 2010), toxicological evaluation (Meerts et al., 2009), and protective effect against gentamicin induced nephrotoxicity (Asadpour et al., 2010).

Pomegranate seed oil can be extracted with various solvents and extraction methods (Abbasi et al., 2008a,b; Eikani et al., 2012). In order to reduce the extraction time and improve the extraction yield, new techniques need to be developed. Ultrasonics is one of the most industrially used methods to enhance mass transfer phenomena (Corrales et al., 2008). The use of ultrasound in food processing has been reviewed by Mason et al. (1996). Ultrasound has been recognized for potential application in the extraction of herbals and oils (carnosic acid, ginseng saponins, carvone, limonene, antraquinones, amaranth oil, gingerols, soybeans oil, almond oil, apricot oil), proteins (soy protein), and bioactive compounds from plant (polyphenols, anthocyanins, tartaric acid, aroma compounds, polysaccharides and functional compounds) or animal (chitin, lutein) materials (Vilkhu et al., 2008). Recently, the design of ultrasound processing equipment has advanced to provide industrially robust processing capability. The proposed benefits include (a) overall, enhancement of extraction yield or rate, (b) enhancement of aqueous extraction processes where solvents cannot be used (juice concentrate processing), (c) providing the opportunity to use alternative (GRAS) solvents by improvement of their extraction performance, (d) enable sourcing/substitution of cheaper raw product sources while maintaining bioactive levels, and (e) enhancing extraction of heat sensitive components under conditions which would otherwise have low or unacceptable yields (Vilkhu et al., 2008).

Extraction enhancement by ultrasound has been attributed to the propagation of ultrasound pressure waves and resulting cavitation forces, where bubbles can explosively collapse and generate localized pressure causing plant tissue rupture and improving the release of intracellular substances into the solvent (Knorr et al., 2002). According to Vilkhu et al. (2008), the implosion of cavitation bubbles generates macro-turbulence, high-velocity inter-particle collisions, and perturbation in micro-porous particles of the biomass, which accelerates the eddy diffusion and internal diffusion. Moreover, the cavitation near the liquid–solid interface sends a fast moving stream of liquid through the cavity at the surface, whereas cavitation on the product surface causes impingement by microjets that result in surface peeling, erosion, and particle breakdown.

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Abbasi et al. (2008a) extracted oil from pomegranate seeds applying ultrasonic irradiation. However, the effects of processing factors on the yield of ultrasound-assisted extraction have not been studied. In addition, the determination of kinetic parameters is very important for designing efficient ultrasound extraction processes. The typical kinetic models of solid–liquid extractions include unsteady diffusion (Stankovic et al., 1994), Fick's law of diffusion (Cacace and Mazza, 2003), film theory (Pekic et al., 1988), and empirical models (Peleg, 1988). However, no information is available for kinetic modeling of pomegranate seed oil ultrasound extraction.

Thus, the objectives of this work were to determine the kinetic parameters that describe the mechanism of pomegranate seed oil ultrasound extraction and to study the effects of various parameters on extraction yield and extraction kinetics.

2. Materials and methods

2.1. Materials

Fresh, good quality pomegranates (Wonderful variety) procured from the local market were used. Pomegranate seeds were separated from the juice and washed carefully to remove sugars and other adhering materials. The seeds were dried at 60 °C for 48 h and kept at −30 °C until use. The seeds were ground in a laboratory mill immediately prior to extraction to produce samples with average particles sizes of 0.2, 1.0, 1.8, 2.6, and 3.4 mm.

2.2. Ultrasound extraction

A 130 W, 20 kHz VCX-130 Sonics and Materials (Danbury, CT, USA) sonicator equipped with a Ti–Al–V probe (13 mm) was used for ultrasound-assisted extraction in pulsed mode. The pulse duration and pulse interval refer to "on" time and "off" time of the sonicator. The amplitude control of the processor allowed the ultrasonic vibrations at the probe to be set at any desired level in the 10–100% range of the nominal power. A sample of pomegranate seeds was mixed with 100 mL hexane to produce different hexane/seed ratios. During the extraction process, the sample container was held in a thermostat-controlled water bath.

In all experiments, the extracts were collected at 2, 5, 10, 20, 30, and 40 min. The resulting extracts were evaporated using a rotary evaporator (Rotovapor R114, Waterbath B480, Büchi, Flawil, Switzerland) and then were dried until a constant weight was reached. The extracted oil in each time step was weighed and recorded as kinetic extraction data at that time. The results were the mean of two replications with the mean relative standard deviation up to 10%. Extraction yield (wt.%), Y, was defined as the percent ratio of the total weight of oil extracted to the sample weight.

The variation of extraction yield during the extraction process (40 min) was studied with various (i) seed particle sizes (S), (ii) extraction temperatures (T_e), (iii) hexane/seed ratios (LS), (iv) amplitude levels (A), and (v) pulse duration/pulse interval ratios (DI). A central composite design was applied to determine the effects and the optimum levels of the above parameters. The effects were studied at five experimental levels −a, −1, 0, +1, and +a. A total of 32 experiments were required as described in Table 1.

2.3. Conventional extraction

A five-gram sample was blended with 20 mL hexane and mixed thoroughly using a magnetic stirrer for 4 h (Abbasi et al., 2008a). The resulting extract was evaporated and then was dried until a constant weight was reached.

2.4. Kinetic model

The solid–liquid extraction process can be considered as the reverse of an adsorption operation, therefore the bases of the adsorption kinetic equations can be applied to solid–liquid extraction and the second-order law was found to give the best fits for the extraction rate (Rakotondramasy-Rabesiaka et al., 2009). The general second-order model can be written as (Pan et al., 2012):

$$\frac{dC_t}{dt} = k \cdot (C_e - C_t)^2 \tag{1}$$

where k is the second-order extraction rate constant (L/g min), C_e is the equilibrium concentration of seed oil in the liquid extract (g/L) (extraction capacity), and C_t is the oil concentration (g/L) in the liquid extract at a given extraction time t.

The integrated rate law for a second-order extraction under the boundary conditions $t = 0$ to t and $C_t = 0$ to C_t, can be written as an Eq. (2) or a linearized Eq. (3) (Qu et al., 2010):

$$C_t = \frac{k \cdot t \cdot C_e^2}{1 + k \cdot t \cdot C_e} \tag{2}$$

$$\frac{t}{C_t} = \frac{1}{k \cdot C_e^2} + \frac{t}{C_e} = \frac{1}{h} + \frac{t}{C_e} \tag{3}$$

where h is the initial extraction rate (g/L min) when t approaches 0:

$$h = k \cdot C_e^2 \tag{4}$$

2.5. Statistical analysis

The data were analyzed using the statistical software MINITAB (Release 13.32). Regression analysis was used to fit a full second order polynomial, reduced second order polynomials, and linear models to the data of each of the variables evaluated (response variables). F values for all reduced and linear models with an $R^2 \geqslant 0.70$ were calculated to determine if the models could be used in place of full second order polynomials to predict the response of a variable to the independent variables.

The reason that a subset of variables rather than a full set would be used is because the subset model may actually estimate the regression coefficients and predict future responses with smaller variance than the full model using all predictors. Typically, R^2 always increases with the size of the subset. Therefore, R^2 is most useful when comparing models of the same size. The square root of mean square error (S') and the Mallows' Cp statistic (Cp) can be used as comparison criteria to compare models with different numbers of predictors. A good model should have a high R^2, a small S', and a Mallows' Cp statistic close to the number of predictors contained in the model.

3. Results and discussion

3.1. Extraction yield

The pomegranate seeds had a yield varied between 302.3 and 446.3 g oil/kg. The achieved values of yields were higher than those reported for other extraction methods (Soxhlet, normal stirring, microwave-assisted extraction, supercritical fluid extraction, cold pressing) (Abbasi et al., 2008a,b; Eikani et al., 2012). Improved oil yields may be explained in terms of cavitational effects caused by the application of high-intensity ultrasound. As large amplitude ultrasound waves travel through a mass medium, they cause compression and shearing of solvent molecules resulting in localized changes in density and elastic modulus. As a consequence, the ini-

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