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Kolkhoung (*Pistacia khinjuk*) kernel oil quality is affected by different parameters in pulsed ultrasound-assisted solvent extraction

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ABSTRACT

In this study, the effect of three amplitudes of pulsed ultrasound-assisted solvent extraction (PUASE) (0, 25, and 50%; 100 W, 30 kHz; the 0% treatment serving as control) on kinetics, yield and quality of extracted oil from Kolkhoung kernel at different temperatures (30, 40, and 50 °C) was evaluated. The highest oil yield, 77.5% (w/w), was obtained for samples treated with PUASE at 50% amplitude and 50 °C. The kinetics of extraction were evaluated based on a second order mechanism. Increases in amplitude and temperature significantly increased initial extraction rate (h), saturated extraction capacity (C_s), and rate constant of extraction (k). The thermodynamic aspects of the extraction process showed that samples treated with PUASE have lower activation energy (E_a), frequency factor (A), enthalpy (ΔH^{++}) and entropy (ΔS^{++}) than control. Ultrasound influenced entropy (or A) more than enthalpy (or E_a) in the rates of oil extraction. However, these values were independent of ultrasound amplitude. Moreover, PUASE did not significantly affect fatty acid composition, peroxide value (PV), conjugated diene value (CDV) and anisidine value (AnV) of extracted oils, but temperature decreased linoleic and linolenic acid content and increased oxidation products of oils. PUASE also increased tocopherols and tocotrienols content of oils but temperature did not significantly affect them. Thus, PUASE increases kinetics and quality of extracted oil and improves extraction process.

1. Introduction

The genus *Pistacia* belongs to the Anacardiaceae, a widely world spread plant family which comprises about 70 genera and over 600 species. *Pistacia khinjuk* Stock which naturally grows in Iran is denominated Kolkhoung in Persian language (Tavakoli et al., 2013). Different parts of this plant have been investigated for various pharmacological activities such as antidiabetic, antitumor, anticholinesterase, antimicrobial and antifungal activity (Taran et al., 2010). In traditional Iranian medicine, *P. khinjuk* was used as helpful remedy for various diseases including stomach discomfort, vomiting, nausea and motion sickness (Dob et al., 2006).

The oil of Kolkhoung (*P. khinjuk* Stocks) kernel is a valuable oil being used in the pharmaceutical industry. Kolkhoung kernel oil is mainly composed of oleic, linolenic, palmitic, linolenic, behenic, lauric, myristic and arachidic acid. In addition, Kolkhoung kernel oil is considered a valuable source of tocopherols and tocotrienols because the tocols content reported for this oil is much higher than that of common oils (Tavakoli et al., 2013).

Although standalone solvent extraction is the industrial standard for the extraction of some vegetable oils, this method requires long treatment times and numerous sample preparation steps prior to the actual extraction process (Wang and Weller, 2006). Therefore, various innovative methods have been suggested, that could be used to assist the solvent extraction process. It is clear from literature that ultrasound-assisted processing has enormous potential as a novel processing method, especially for oil extraction, a process that has traditionally been based on the use of chemical solvents with the assistance of heat and/or agitation. The mechanical effects of high-intensity ultrasonic cavitation have been found to be ideal for the disruption of most biological cells with rigid cell walls, such as plant cells (Feng et al., 2008; Da Porto et al., 2013). This treatment is considered to be beneficial due to its reduced processing time with lower energy consumption and being environmentally friendly (Long et al., 2011). Using pulsed ultrasound-assisted solvent extraction (PUASE) allowed the suspension to cool down

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temporarily between treatment pulses. This offered more control of the suspension temperature. This was also reported by a recent study that compared pulsed and continuous ultrasonic treatments for the extraction of antioxidants from pomegranate peel (Pan et al., 2011). Moreover giving comparable antioxidant yields, their study also found that pulsed ultrasonic extraction had 50% more energy savings than continuous ultrasonic extraction. Ultrasound treatment has been used for the successful extraction of oils from a diversity of biological materials including sunflower and rapeseed (Luque-García and Luque de Castro, 2004), and almond and apricot (Sharma and Gupta, 2004) among others. Clearly, the extraction of Kolkhoung kernel oil is a process that shares a unique level of economic importance due to their noteworthy nutritional and pharmacological potential. The use of PUASE in the production of this oil may improve efficiency, yield, and quality of Kolkhoung kernel oil compared with conventional methods. The objectives of the present study were to investigate the effect of the amplitude of PUASE and extraction temperature on the kinetics and quality of extracted oil from Kolkhoung kernel.

2. Materials & methods

2.1. Kolkhoung kernels and chemicals

Dried Kolkhoung (*P. khinjuk* Stock) fruits (12% moisture content/dry basis, 10 kg) were purchased from the local market in Yasooj city in February 2014 and stored at −18 °C until initiation of the experiments. After separation of the hull, kernels were ground into powder using a grinder and passed through a standard sieve to select particles smaller than 1.18 mm. All chemicals and solvents used in this study were of analytical reagent grade and purchased from Merck and Sigma Chemical Companies.

2.2. Methods

2.2.1. Oil extraction process and treatments

For PUASE, a Hielscher ultrasonic device (UP100H, 100 W, 30 kHz) with a titanium sonotrode (tip diameter10 mm) was used. The effects of three levels of amplitude (0, 25, and 50%) at three temperatures (30, 40, and 50 °C) were investigated. The 0% amplitude experiment was the control; basically, ultrasonics was not turned on and the sample-solvent mixture was undisturbed during the process.

Ground Kolkhoung powder was mixed with *n*-hexane at ratio of 1:4 (w/v). Ultrasound treatment was applied to the sample by inserting the probe approximately 5 cm from the top into the sample-solvent suspension in the cell. The ultrasonic treatment was applied in pulses of 10 s duration separated from each other by 5 s of resting time. To avoid significant solvent evaporation that could potentially occur at long treatment periods and/or at higher amplitudes, a special evaporation-proof cap was used during the ultrasonic extraction process. A water bath was used to maintain the temperature of the extraction medium at 30, 40 and 50 °C during the process. In addition, the temperature of the medium was monitored every 20 min to ensure that there was no temperature over run. Each experiment was carried out in triplicate. After ultrasonic extraction, the sample-solvent suspension was allowed to sit at room temperature for 10 min; the supernatant was then decanted into a separate tube and the residue was washed twice with 5 mL of *n*-hexane. Next, 15 mL of 10% sodium sulphate solution was added to the decanted suspension, separating it into two phases: an upper hexane phase containing the extracted lipids and a lower phase containing all the other cellular components. Phase separation was made more distinct by centrifugation at 4000 × *g* for 10 min. The upper hexane phase was then aspirated into a pre-weighed stainless steel vessel and dried over a stream of nitrogen for 2–3 h until constant weight.

2.2.2. Determination of oil yield

The oil yield (Y) was determined gravimetrically:

$$Y(\%) = \frac{m_o}{m_k} \times 100$$

Where m_o is the mass of extracted oil (*g*) and m_k the mass of ground Kolkhoung kernel (*g*).

2.2.3. Kinetics and thermodynamic parameters

The extraction rate can be written as the following Eq. (1):

$$\frac{Ct}{t} = \frac{1}{1/k(Cs)2} + \frac{1}{t/Cs} \quad (1)$$

where k = The second-order extraction rate constant (L/g min); Cs = The extraction capacity (concentration of oil at saturation in g/L); C_t = The concentration of oil in the solution at any time (g/L), t (min)

Then, when t approaches 0, the initial extraction rate, h, can be written as:

$$h = kC_s^2 \quad (2)$$

By rearrangement of Eq. (1), the concentration of oil at any time can be obtained as:

$$Ct = \frac{t/1}{h} + \frac{t/t}{C_s} \quad (3)$$

The initial extraction rate, h, the extraction capacity, Cs and the second order extraction constant, k, can be calculated experimentally by plotting t/Ct versus t (Sayyar et al., 2009).The effect of temperature on the rates of extraction was evaluated by means of the Arrhenius equation:

$$logk = \log A - \left(\frac{Ea}{2.303RT}\right), \quad (4)$$

where k (h^{-1}) is the reaction rate constant, R is the molar gas constant (8.3143 J/mol K), T is the absolute temperature (K), E_a is the activation energy (kJ/mol) and A (h^{-1}) is the pre-exponential factor.

Enthalpies (ΔH^{++}) and entropies (ΔS^{++}) of activation were determined by regressing log k/T versus the inverse of temperature (T, K) via the equation derived from the activated complex theory:

$$\log\left(\frac{k}{T}\right) = \log\left(\frac{kB}{h}\right) + \left(\frac{\Delta S^{++}}{2.303R}\right) - \left(\frac{\Delta H^{++}}{2.303RT}\right), \quad (5)$$

where k_B is the Boltzmann constant (1.380658×10^{-23} J/K, the ratio between R and Avogadro's number, 6.022×10^{23} mol^{-1}) and h is the Planck's constant ($6.6260755 \times 10^{-34}$ Js). From the slopes and intercepts of the lines, the values of $\Delta H^{++}$and ΔS^{++}were calculated.

2.2.4. Analysis of tocopherols and tocotrienols by HPLC

The content of tocopherols and tocotrienols in the kernel oils of Kolkhoung were determined using a high performance liquid chromatography (HPLC) (Waters, Alliance system, USA) with a Spherisorb column (25 cm 4 mm i.d., Waters, USA) packed with silica (5 m particle size) and a fluorescence detector operating at an excitation wavelength of 290 nm and an emission wavelength of 330. The mobile phase was hexane–isopropanol (98.5:0.5, v/v) at a flow rate of 1 mL/min. The tocopherols and tocoterienols in the test samples were verified by comparison of their retention times with those of reference standards (ISO 9936, 1997).