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Ultrasound assisted supercritical fluid extraction of oil and coixenolide from adlay seed

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Abstract

Oil and coixenolide are important components of adlay seed (*Coix lachrymal-jobi L. var. Adlay*) with many beneficial functions to human health. In this work, a novel extraction technique—ultrasound assisted supercritical fluid extraction (USFE)—was studied. Effects of operating conditions on the extraction, including extraction temperature (*T*), pressure (*P*), time (*t*), CO_2 flow rate (*F*) and ultrasonic power (*I*) were investigated. There are optimum temperatures which gives the maximum extraction yields (EYs) for the supercritical fluid extractions with and without ultrasound. The effect of pressure on EYs for is similar to that of pressure on CO_2 density. Based on the yield of extraction, the favorable conditions for supercritical fluid extraction (SFE) were: *T* at 45 °C, *P* at 25 MPa, *t* at 4.0 h and *F* at 3.5 L/h. While ultrasound was applied as in USFE, the following parameters were preferred: *T* at 40 °C, *P* at 20 MPa, *t* at 3.5 h and *F* at 3.0 L/h, respectively. The results show that supercritical fluid extraction with the assistance of ultrasound could reduce the temperature, pressure, CO_2 flow rate, as well as time used in the process. Compared with SFE, USFE could give a 14% increase in the yield for extracting oil and coixenolide from adlay seed with less severe operating conditions.

Keywords: Supercritical fluid extraction; Ultrasound; Oil; Coixenolide; Adlay seed

1. Introduction

Wild *coix lachrymal-jobi L.* (Coix) is native to and extensively grown in South Asia [1]. The cultivated variety, *coix lachrymal-jobi L. var. adlay* (Adlay), is a soft-shelled seed crop cultivated in countries such as India [1], Brazil [2], Japan [3] and China [4]. Adlay has long been used as animal feed, as food for humans and in herbal medicine. Adlay oil and coixenolide are important components of adlay seed with many health benefits. Adlay oil can inhibit the growth of cancer cells with an efficiency of above 87%, and help prevent the decrease of white blood cells during chemical therapy [5]. Coixenolide has a stimulatory effect on lung, heart, striated muscle and smooth muscles with low dosage, but an inhibitory effect with high dosage. It can dilate the pulmonary veins and improve the blood circulation of the lung [6]. In addition, coixenolide has the effect of reducing inflammation, purulence and pain as well as being anti-tumor.

Adlay oil and coixenolide are normally obtained using mechanical or chemical processes. Mechanical processes often associate with low yields, while chemical extraction methods often involve the use of organic solvents which can be harmful to human health and environment [7]. Tough new regulatory requirements on the use of organic solvents have prompted active research on clean extraction technologies [8]. Supercritical fluid extraction is one of the

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newly emerging clean and environmentally friendly technologies for food and pharmaceutical products [9].

Among supercritical fluids, CO_2 is the most commonly used solvent for the extraction of oils from natural products. However, the efficiency of supercritical fluid extraction (SFE) is hindered by the low solubility of the triglycerides in CO_2, and the high pressures and long extraction time required [8].

Recently, the application of ultrasound techniques in solvent extraction has attracted more attention. Sonication has been used successfully to isolate pharmaceutically active components from *Salvia officinals*, and increase the yield of xylems from corn hulls [10] and corn cobs [11]. The solvent extraction of active components from plants and seeds was found to be significantly improved by the introduction of ultrasound waves, and extensive researches on ultrasound assisted solvent extraction have been conducted. However, the application of ultrasound in supercritical fluid extraction is still in the developing era. More recently the use of power ultrasound in SFE to enhance the extraction yield of oil from almonds by 20% was reported [12].

The main objective of this work is to extract adlay oil and coixenolide using the ultrasound assisted supercritical fluid extraction (USFE). The results obtained from USFE will be compared with that obtained from the SFE to reveal the effects of ultrasound under supercritical conditions.

2. Materials and methods

2.1. Materials

Adlay seeds were bought from the local traditional Chinese medicine shop. The oil content of the adlay seed, as determined by extraction with acetone, was found to be 9.5%. CO_2 of 99.9% purity was obtained from Guangzhou Gas Company, China. All chemicals were purchased from local chemical stores and at analytical grades.

2.2. USFE system

As showed in Fig. 1, the USFE system is made up of two units: SFE unit and ultrasonic unit. The USFE extractor is designed to withstand pressures up to 32 MPa and temperatures up to 85 °C. The major components of SFE include a positive displacement liquid pump, a 1000 ml pressurized extraction vessel, a separation column and a separation vessel. The extraction vessel and two separators are equipped with water jackets and temperature controllers. In order to ensure accurate and stable supercritical CO_2 delivery, the pump head is cooled by circulating water. The temperatures in the system are controlled within ±0.1 °C and the pressures within ±0.5 MPa.

The probe with Langevin type transducer is installed in the upper part of the extractor, and driven by electrical signals from an ultrasound generator, which gives adjustable continuous power outputs at fixed frequency of 20 kHz. The transducer can stand for a maximum temperature of 105 °C. The ultrasound generator consists of a power amplifier and a special electro circuit designed to justify the power outputs at a constant level during the USFE process. The ultrasonic power outputs were set at 0, 50, 91, 97 and 110 W in this study, respectively, and kept at a constant level with minor fluctuation caused by minor oscillating static pressure and CO_2 flow rate when supercritical fluid was pumped into the extractor during the process. The electro-acoustical efficiency of the ultrasonic transducer was 87%.

2.3. Experimental methods

In order to fully explore the effects of USFE, experiments were carried out at various extraction temperatures (30–55 °C), pressures (10–30 MPa), times (up to 4.5 h) and CO_2 flow rates (1.5–4 L/h). 100 g of grounded adlay seed of 0.3–0.45 mm in diameter was placed into the extractor in a typical extraction experiment. Liquid CO_2 was pumped into the extractor until the desired extraction pressure was reached. The extractor was heated to the extraction temperature, and pressure valves located downstream of the extractor were slowly opened while maintaining the pressure constant in the extractor.

2.4. Calculation of adlay oil extraction yield

The adlay oil, which precipitated under a low pressure and temperature in the separation vessel, was recovered. The adlay oil extraction yield (EY) is calculated using the following formula:

$$\mathrm{EY} = \frac{M_t}{M_0 X_0} \times 100\% \tag{1}$$

where M_t is the mass of extracted adlay oil (mg), M_0 the initial mass of adlay seed put into the extractor, X_0 the initial adlay oil content of raw adlay seed (mg/mg).

2.5. Measure of the coixenolide

1.3 g extracted adlay seed oil was placed into a 250 ml conical flask with 25 ml solution of potassium hydroxide in ethanol (0.5 mol/L), and refluxed for 30 min. After cooling, 10 ml ethanol was used to wash the wall of the condenser and the under-stopper. 1.0 ml phenolphthalein was added into the solution. To measure the remaining potassium hydroxide, hydrochloric acid (0.5 mol/L) was gradually added until the solution just turn from red to colorless. A blank was prepared in the same way without adlay oil. The coixenolide content is found by using the following equation:

$$\mathrm{Coixenolide}(\%) = [(B - A) \times G_1 \times 10^3/G_0] \times 100\%$$

where A is the volume of hydrochloric acid consumed by the sample (ml), B the volume of hydrochloric acid consumed by the blank (ml), G_1 the quantity of coixenolide re-