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Acidic pH based microwave-assisted aqueous extraction of seed oil from yellow horn (*Xanthoceras sorbifolia* Bunge.)

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ABSTRACT

In this study, an efficient and green acidic pH based microwave-assisted aqueous extraction (MAAE) of seed oil extraction from yellow horn (*Xanthoceras sorbifolia* Bunge.) was investigated. It was observed that oil extraction yield increased at weak acidic condition, and the pH effects on the oil extraction process were illustrated. Meanwhile, the operating parameters were optimized using central composite design (CCD) combined with response surface methodology (RSM). From the economic perspective, the selected operating parameters were: pH 5, microwave power 500 W, stirring rate 300 rpm, extraction temperature 70 °C, liquid to solid ratio 5.2:1 and extraction time 52 min. The physicochemical properties were determined to evaluate the quality of seed oil. The chemical composition of extracted seed oil was analyzed by GC–MS. This novel extraction technique provided high throughput and high quality oil.

1. Introduction

Yellow horn (*Xanthoceras sorbifolia* Bunge.), belonging to the Sapindaceae family, is an important oil crop in China because of the abundant oil content (55–65%) in the seed kernels (Zhang et al., 2010). Yellow horn seed oil is rich in unsaturated fatty acid (UFA) (85–93%) and most of the UFA is linoleic acid. Linoleic acid is an essential fatty acid which cannot be synthesized in the body, it is present in the diet (Pomeranz, 2003). High content of linoleic acid is favorable for medicinal and nutritional application since it is responsible for cardio-protective, antidiabetic, antimicrobial activities (Szentmihályi et al., 2002). Thus, yellow horn seed oil can be refined as nutritional edible oil. Therefore, the investigations on efficient extracting seed oil from yellow horn are greatly significant for the utilization of this oil resource.

Extraction holds the key to the recovery of oil yield from plant seed materials. Many extraction methods have been employed to extract oil from plant seeds. The traditional plant oil extraction methods include expeller pressing and organic solvent extraction. However, the former process used in industrial scale is of high energy consumption, high level equipment and low extraction yield. The latter process may produce an effluent disposal which leads to environmental problems and economical inconveniences. Hence, there has been an increasing demand for efficient and green process techniques (Grosso et al., 2008; Passos et al., 2009). Recently, a novel aqueous extraction of plant oil has attracted considerable interests, since it is more efficient and highly selective, involves less energy consumption, and produces fewer wastes. Not only pollution and hazards are eliminated at the source in this process, but also environmental impact and costs are reduced. However, a major problem with aqueous extraction is the incomplete oil extraction of the water compared with organic solvents. Therefore, it is necessary to find a suitable method to increase the extraction yield so as to promote the application of aqueous extraction technique.

As a new-type extraction technique, microwave-assisted extraction (MAE) has been accepted as a potential and powerful alternative to conventional extraction techniques (Eskilsson and Björklund, 2000). Compared with conventional extraction methods, MAE has many advantages, such as shorter extraction duration, higher extraction yield and lower energy input (Yan et al., 2010). Furthermore, according to previous research, denaturation or aggregation of proteins was caused by pH effects (Khalid et al., 2003), which might be utilized for separating oil from proteins in extraction process. It is noteworthy that the combination of microwave irradiation and pH effects may exhibit somehow synergistic effects on enhancing the oil quality and efficiency in the

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aqueous extraction. However, little research has been done so far on the establishment of novel green technique for plant oil extraction and the pH effects in the aqueous process assisted by microwave irradiation.

Thus, the microwave-assisted aqueous extraction (MAAE) under varying pH conditions was developed to extract seed oil from yellow horn in this study. The conventional seed oil extraction methods were inefficient and not friendly to environment. But the MAAE may overcome those disadvantages. This study described the potential use of microwave and pH effects in the aqueous extraction for the first time. Hence, the objective of this study was to optimize MAAE of seed oil, which might provide valuable data for green and economic process design and pilot-scale, and the pH effects were evaluated. Extraction variables consisted of extraction temperature, liquid to solid ratio and extraction time. Response surface methodology (RSM), an ideal tool for process optimization, was used for the optimizing extraction process. Furthermore, the physicochemical properties of the oil were estimated in order to investigate its quality, and the chemical composition of the extracted seed oil was analyzed by GC–MS.

2. Materials and methods

2.1. Materials and reagents

Seeds of yellow horn (*X. sorbifolia* Bunge.) were collected in the autumn of 2010 from Inner Mongolia Autonomous Region, China, and identified by Prof. Shao-Quan Nie, Key Laboratory of Forest Plant Ecology, Ministry of Education, Northeast Forestry University, Harbin, China. Yellow horn seeds were cracked and the seeds were collected. Then the kernels thus obtained were milled into grains for oil extraction. All chemicals and solvents used were purchased from Kermel Chemical Reagents Company (Tianjin, China) and were analytical grade.

2.2. MAAE under varying pH conditions

MAAE under varying pH conditions was carried out using a device supplied from SINEO Microwave Chemistry Technology (Shanghai, China) equipped with a TFT multicolor liquid-crystal screen, a power sensor (the power range 0–1000 W), an infrared temperature sensor, a temperature controller, a special three necks round-bottomed flask, and mechanical stirrer. In brief, the operating methodology was as follows: firstly, the amount of acid in the extraction solvents was regulated at initial pH from 3 to 6 by using 0.1 M hydrochloric acid solution. The ultra-pure water (pH 7) was used as control. According to the pH of extraction solvents, two modes were founded as MAAE (ultra-pure water), acidic pH based MAAE (acidic water). Then, ten grams of material after cracked and extraction solvent of specified volume were added into the extraction flask. The MAAE device was turned on, and the preliminary conditions including extraction temperature, microwave power and extraction time were set by the digital panel. When the scheduled time was achieved, the mixture obtained was transferred into a centrifuge tube. Then, the upper oil phase was collected and the suspension phase was removed for reuse of proteins. After collected, the oil phase was centrifuged at 8000 rpm for 10 min. The amount of extracted oil was determined gravimetrically after collection, and then the extraction yield was expressed as the percent ratio of the mass of extracted oil to the mass of yellow horn seed loaded in the extraction vessel, as follows:

$$\text{Extraction yield of seed oil}(\%) = \left(\frac{\text{mass of extracted oil}}{\text{mass of dried material}}\right) \times 100$$

2.3. Experimental design

To obtain appropriate extraction conditions for yellow horn seed oil, a series of studies were conducted to investigate microwave-assisted aqueous extraction under varying pH conditions. The investigated parameters included varying pH, extraction temperature, liquid to solid ratio and extraction time. For the prevention of splashes caused by rapid heating, the microwave power and stirring rate were selected at 500 W and 300 rpm, respectively.

The varying pH was studied by using single-factor experiment, which ignored the interactions between the different extraction parameters. To procure the appropriate pH, five different pH values in ultra-pure water from 3 to 7 were investigated. Ten grams of yellow horn seed kernels were extracted using the microwave device at extraction temperature 60 °C, liquid to solid ratio 5:1 for 60 min.

The other three factors, extraction temperature, liquid to solid ratio and extraction time, were investigated using central composite design. In statistics, a central composite design (CCD) is an experimental design, which is useful in response surface methodology, for building a second order (quadratic) model for the response variables without needing a complete five-level factorial experiment. Consequently, with regard to optimizing the other three factors, a 2^3 factorial portion CCD with RSM was applied to determine the most appropriate combination of extraction variables for the oil extraction yield from yellow horn. As shown in Table 1, the effects of three parameters on the oil extraction were studied at five levels. The coded variables calculated by the following equation (Banik and Pandey, 2008):

$$\text{Coded level} = \frac{\text{actual level} - (\text{high level} + \text{low level})/2}{(\text{high level} - \text{low level})/2}$$

CCD consisting of 14 experimental runs with three replicates at the center point was shown in Table 1. All the experiments were conducted in random order to minimize the effects of unexplained variability in the observed response due to extraneous factors. The experimental data were fitted with a second-order polynomial model, which have the following form:

$$Y = \beta_0 + \sum_{i=1}^{k}\beta_i X_i + \sum_{i=1}^{k}\beta_{ii}X_i^2 + \sum_{\substack{i=1\\ i<j}}^{k-1}\sum_{j=2}^{k}\beta_{ij}X_iX_j (k=3)$$

where Y was the responses function; X_1, X_2, and X_3 were the independent variables affecting the response function Y; β_0, β_j, β_{jj} and β_{ij} were the regression coefficients for intercept, linearity, square and interaction terms, respectively; k represented the number of variables.

2.4. Evaluation of physicochemical properties

American Oil Chemists' Society (AOCS) standard methods were used to evaluate the main properties of yellow horn seed oil.

2.4.1. Acid value of oil

Acid value was determined following the AOCS Official Method Cd 3d-63. Three replicates were performed for each test sample.

2.4.2. Iodine value of oil

Iodine value was evaluated using the AOCS Official Method Cd 1–25. Three replicates were performed for each test sample.

2.4.3. Peroxide value of oil

Peroxide values were measured by the AOCS Official Method Cd 8b-90. Three replicates were performed for each test sample.