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A process to acquire essential oil by distillation concatenated liquid-liquid extraction and flavonoids by solid-liquid extraction simultaneously from *Helichrysum arenarium* (L.) Moench inflorescences under ionic liquid-microwave mediated

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ABSTRACT

An efficient ionic liquid-mediated microwave-assisted hydrodistillation concatenated liquid-liquid extraction (ILMHDE) technique was developed for distillation of essential oil and extraction of non-volatile flavonoids (astragalin, quercetin, luteolin, kaempferol and apigenin) from the inflorescences of *Helichrysum arenarium* (L.) Moench. In addition to collecting essential oil on the top of hydrosol in the conventional oil-water separation process, another extraction process was realized for extracting some essential oil components from the hydrosol using a small amount of organic solvents, which can effectively reduce the organic content in wastewater and its further disposal burden. Through comparison, 1.0 M [C_8mim]Br was selected for the extraction and distillation in a sample reaction flask, and ethyl ether was chosen as the extraction solvent in the second separation column. Based on the yields of total essential oil and total flavonoids, the ILMHDE process parameters (liquid-solid ratio, microwave irradiation time, microwave irradiation power) were optimized via the Box–Behnken design. Due to the combined effects of the microwave irradiation, the addition of ionic liquid and the modified hydrodistillation concatenated liquid-liquid extraction apparatus, greater advantages were found in the ILMHDE process compared with other traditional methods, as evidenced by the extraction kinetics. After the GC–MS analysis, a higher content of oxy-components was detected in the essential oil that was separated in the second separation column than that in the first one, and a more valuable essential oil was achieved. Therefore, the ILMHDE technique is a good alternative for simultaneous distillation of essential oil and extraction of non-volatile components from medicinal plants.

1. Introduction

Helichrysum arenarium (L.) Moench, a perennial herbaceous plant that belongs to the Asteraceae family, is broadly distributed in Europe, western Siberia, and central Asia. In China, *H. arenarium* has been widely cultivated as an industrial crop in the northern areas. Much research has been performed to study the essential oil (EO) or extract of *H. arenarium* [1–3] because of its valuable pharmacological activities [5,6]. The inflorescence of *H. arenarium* has been used for a long time in folk medicine, mainly due to its bioactivities, including antimicrobial [7,8], antioxidant [9], antiradical [2], hepatoprotective [10] and detoxifying activities [2]; moreover, it has been used in the cosmetics industry for its fragrance [11]. Some pharmacological data indicate that the inflorescence of *H. arenarium* is rich in flavonoids [12] and EOs [13]. In many cases, pharmacological activities are influenced by the presence and content of these active ingredients. Therefore, developing an efficient method to separate the active ingredients from the inflorescences of *H. arenarium* is significantly meaningful.

Flavonoids are secondary metabolites with low molecular weights, are one of the most numerous and widespread groups of phenolic constituents in medicinal plants, and they possess many biological and pharmacological activities [14,15] due to their phenolic structures. Flavonoids are the most important active components in the inflorescences of *H. arenarium*, including astragalin, luteolin, kaempferol, etc. [16]. Plant EOs, which are natural products, are considered to be non-toxic compounds, and they have been used as natural conservation agents either alone or in combination with other preservatives [17]. In addition, the EO isolated from the inflorescences of *H. arenarium* has been confirmed to have better antimicrobial activities [18]. Therefore, increasing attention should be paid to these natural compounds due to

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their potential applications and economic value.

The most traditional method for isolating EO from plant materials is hydrodistillation (HD). However, this method is always accompanied by some disadvantages, including lengthy duration, low extraction efficiency, and loss of some components due to degradation and isomerization under prolonged high temperature treatment [19]. Due to the high demand for using high quality EO in the food, pharmaceutical and cosmetics industries, much attention has been paid to the development of a new technique with high efficiency and short time consumption. Driven by these goals, microwave-assisted hydrodistillation (MHD) has emerged. The procedure, which is based on microwave irradiation, provides a number of advantages for EO separation because microwaves are easy to use, fast, and can control the process via small heating increments [20], all of which contribute to low environmental impact and costs [19]. Moreover, based on these advantages, the microwave-assisted procedure has also replaced other conventional techniques for extraction of non-volatile components from plant materials over the years [21,22]. Traditionally, extraction and isolation of EO and non-volatile components has been realized in individual procedure, which is time-consuming and inefficient. Thus, the application of the MHD technique for the simultaneous isolation of EO and non-volatile components from the inflorescences of *H. arenarium* should be researched in depth.

Water is the most commonly used solvent for distilling EO. However, the dissolution of non-volatile components in water is relatively poor. Thus, finding a suitable solution with both the distillation characters of water and the better dissolving capacity of non-volatile components is a critical step. In recent years, the application of ionic liquids has attracted wide interest in the extraction process due to their specific properties, including negligible vapor pressure, tunable viscosity, good stability and miscibility with water and organic solvents, and good solubility and extractability for a series of active compounds [23–25]. In addition, the strong ability of ionic liquids to absorb and transfer microwaves results in many advantages for the application of ionic liquids under microwave irradiation [26]. In previous research, ionic liquids have been considered as alternatives to commonly used solvents in some applications, especially in extraction and separation science[24,27,28]. Therefore, the use of ionic liquid-water as the solution for the distillation of EO and extraction of non-volatile components from the inflorescences of *H. arenarium* is worth studying.

A traditional Clevenger apparatus, which is used in HD and MHD procedures to obtain EO, is based on the separation of EO on the top of condensate water. However, a small amount of essential oil components often forms a hydrosol with condensate water, which is not easy to separate and collect. An apparatus for distillation and separation of EO from aromatic plant materials have designed [29], based on the traditional Clevenger apparatus. In this work, the developed apparatus combined with microwave irradiation was used for the simultaneous distillation and extraction of EO and non-volatile flavonoids, such as astragalin (AG), quercetin (QC), luteolin (LT), kaempferol (KF) and apigenin (AP), from the inflorescences of *H. arenarium* using an ionic liquid solution as the extraction solvent, namely, ionic liquid-mediated microwave-assisted hydrodistillation concatenated liquid-liquid extraction (ILMHDE). The modified apparatus consists of two separation processes for EO. The first one is the conventional oil-water separation process, and the second one is the extraction process of EO components from the hydrosol using an organic solvent. Thus, the EO components dissolved in hydrosol can also be separated, which improves the separation efficiency of EO and takes full advantage of raw material resources. In addition, using a small amount of organic solvents for extraction of some essential oil components from hydrosol in the second separation column can effectively reduce the organic content in wastewater, thus reducing the further disposal burden of wastewater produced. The parameters that influence the process were systematically optimized. Moreover, the ILMHDE procedure was compared with the traditional HD, MHD and HRE techniques.

2. Experimental

2.1. Materials and chemicals

The aerial part of *H. arenarium* was hand-harvested during flowering from Alax in Inner Mongolia, China, which was authenticated by Prof. Guangming Du from the College of Animal Science and Veterinary Medicine, (Heilongjiang Bayi Agricultural University, China). The inflorescences of *H. arenarium* were parted off from the aerial part, dried naturally at room temperature, milled in a blender, sieved (40–60 mesh) and stored in closed desiccators until use. The same batch of inflorescences was used in all the following experiments.

Reference standards of AG, QC, LT, KF and AP were bought from Sigma-Aldrich Inc. (St. Louis, MO). Methanol and phosphoric acid (chromatographic grade) for the HPLC analysis were purchased from J &K Chemical Ltd. (Beijing, China). Ethyl ether, *n*-hexane, petroleum ether (303.15 ± 333.15 K), cyclohexane, and anhydrous sodium sulfate were bought from Sinopharm Chemical Reagent Co., Ltd. (Beijing, China). All ionic liquids ([C_2mim]Br, [C_4mim]Br, [C_6mim]Br, [C_8mim]Br, [C_{10}mim]Br, [C_4mim]BF_4, [C_4mim]Cl, [C_4mim]HSO_4, [C_4mim]NO_3, [C_4mim]Ac, and [C_4mim]ClO_4) were bought from the Chengjie Chemical Co., Ltd. (Shanghai, China). All sample solutions were prepared using reverse osmosis Milli-Q water (Millipore, Billerica, USA). Prior to the HPLC analysis, a 0.45-μm microporous membrane (Guangfu Fine Chemicals Research Institute, Tianjin, China) was used to filter all the extraction solutions.

2.2. Apparatus

As seen in Fig. 1, the hydrodistillation concatenated liquid-liquid extraction apparatus was modified based on a traditional Clevenger apparatus. The new apparatus consisted of two separation columns. The first one is the conventional oil-water separation column, and the second one is the extraction column for EO components from hydrosol using an organic solvent.

A domestic WP700 microwave oven (Glanz Electrical Appliance Industrial Co., Ltd., Guangdong, China) was used for the ILMHDE process, with an irradiation frequency of 2.45 GHz. The microwave irradiation power was continuously adjustable (output power from 120 W to 700 W), and the interior cavity size was 215 mm × 350 mm × 330 mm.

2.3. Ionic liquid-mediated microwave-assisted hydrodistillation concatenated liquid-liquid extraction

In total, 50.0 g of *H. arenarium* inflorescences was weighted accurately into a 1-L round-bottom flask containing a certain volume of ionic liquid-water solution of various types and concentrations. Then, the sample flask was put into the microwave oven and connected to the hydrodistillation concatenated liquid-liquid extraction apparatus through the hole that was made at the top of the microwave oven. Prior to distillation, 2 mL of different types of organic solvents was added to the second separation column to extract some of the components from the hydrosol. When the sample mixture started to boil, the distillation and extraction process was continued for a period of time under various microwave irradiation powers. At the boiling temperature, EO could be released and evaporated using water vapor, and then condensed and separated on top of the hydrosol in the first separation column. When the hydrosol reached a certain level after the separation, hydrosol would return to the second separation column, and some hydrosol components could be extracted using an organic solvent.

After the distillation and extraction, the EO, which was obtained in the first separation column, was collected, dried using an anhydrous sodium sulfate, and stored. The extraction solvent in the second separation column was dried using an anhydrous sodium sulfate and concentrated to remove solvents under reduced pressure. The obtained