Recovery of some elements from Empetrum nigrum L. growing in the Kola Peninsula using acid-based deep eutectic solvents

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Abstract. Empetrum nigrum L. (crowberry) is a useful berry plant growing in the Polar region, in particular in the Kola Peninsula. Crowberry berries and leaves are both used in food, beverage, pharmaceutical, and cosmetic production. Developing extraction techniques for such plant raw materials processing is very actual and needs comprehensive study. Commonly, studies are focused of determination of the bioactive components in extracts, but for application it is important to know micro-, macro-, and toxic elements containing in obtained extracts. One of the modern methods of extraction is applying deep eutectic solvents. In this research extracts of E. nigrum L. were obtained using mixtures of choline chloride and malonic, malic, tartaric and citric acids with 30 wt.% of water. Mass-spectrometry with inductively coupled plasma was used for estimation of various metals recovery from plant material. It is obtained that extracts based on deep eutectic solvents are characterized by low concentrations of toxic and rare metals, and relatively high concentrations of macro- and micro-nutrient metals.

1. Introduction

Empetrum nigrum L. (crowberry) is a useful berry plant growing in the Polar region, in particular in the Kola Peninsula. These berries are widely used in traditional recipes of the peoples of the north for making jams and drinks, in folk medicine as a remedy for various diseases. Crowberry fruits contain high amounts of flavonoids [1-3] that demonstrate antioxidant, antimicrobial, and other health promoting activities. Extracts of crowberry have the protective actions against ultraviolet and radiation in human cells. Recent phytochemical studies have shown the presence of new compounds in crowberry leaves [4]. Thus, the development of extraction techniques of crowberry processing is important for both fundamental science and industry and needs comprehensive study.

One of the promising approach in the extraction of bioactive components from plants relates to the using of deep eutectic solvents (DES) [5]. DESs consist of a hydrogen bond donor (HBD) and a hydrogen bond acceptor (HBA). HBD can be organic acids, polyols, sugars, etc. Quaternary ammonium salts, e.g. choline chloride, are HBA. DESs have some advantages, such as low cost, low toxicity, low volatility, high biodegradability. Also, DESs can extract various inorganic compounds include metals from plants [7]. Most of the scientific works focused on the analysis of organic compounds recovery, but the ability to recover macro-, micro-, and toxic elements is also interesting for study. These data can be useful to establish the ability of DESs to extract certain metals from plant materials and to assess the applicability of DESs in the production of natural extracts for industry.
The aim of this work was to study recovery of various metals from E. nigrum L. using acid-based DES.

2. Materials and methods

2.1. Materials

Aerial parts of E. nigrum L. were collected in the valley of Maliy Woodyavr lake, dried on air, and stored in accordance with the rules for drying and storage of vegetable medicinal raw materials [7]. Before extraction plant material was powdered, and a fraction of 0.1 – 0.5 mm was taken.

Choline chloride (99%, RONGSHENG BIOTECH) was used as an HBA for DES, malonic, malic, tartaric, and citric acids (99.0%, Vekton) were used as HBDs. Distilled water was used as an addition to DES.

For the ICP-MS measurements nitric acid after purification by isothermal distillation system Berghof-BSB-939-IR (Berghof, Germany), and deionized water obtained with water purification system «Millipore Element» (Millipore, USA) were used.

2.2. Extraction procedure

DES-based extractants were prepared by mixing choline chloride and HBDs in molar rations 1:1 in the case of HBS is malonic, malic, or citric acid, or 2:1 if HBD is tartaric acid. 30 wt.% of water were added and the mixtures were heated at 60°C until the transparent liquids were formed.

Ultrasound-assistant extraction was performed using Vilitech VBS-3DP ultrasound bath at 45°C. Powdered dried plant material and the extractants were mixed in mass/volume ratio 1:10 in the sealed plastic tubes and were held in an ultrasound bath for 3 hours. After these extracts were centrifuged at 4 krpm for 5 minutes and supernatant was collected.

2.3. ICP-MS measurements

All samples were dissolved in 2 % purified nitric acid. Berhof BSB-939-IR distillacid (Berhof, Germany) was used to facilitate distillation of acids. Millipore Element system (Millipore, USA) was applied to distill water. The content of elements in the samples was measured using a mass spectrometer with an inductively coupled argon plasma ELAN 900 DRC-e (Perkin Elmer, USA). Multi-element ICP-MS Calibration Standard STD 1 (SCP Science, USA) was used for equipment settings. Calibration was made using ICP-MS Calibration Standard IV-STOCK-21, IV-STOCK-26, IV-STOCK-28, IV-STOCK-29 (Inorganic Ventures, USA) with detected elements concentration 10 mg/l, ARD is less then 0.5% at P = 0.95.

3. Results and discussion

Firstly, the data about all possible metal, boron and phosphorus content in the plant material were obtained. Only elements with relatively high concentration (more than 1 ppm) were selected for further consideration. Totally 16 elements were selected (table 1). Plant material contains relatively high amount of potassium, calcium, phosphorus, magnesium, silicon and aluminum. In addition, relatively small amounts of iron, manganese, strontium and barium were found in plant materials. The lowest content was obtained for copper and nickel.

Extraction procedure was made using four acid-based DES: choline chloride + malonic acid 1:1 (DES1), choline chloride + malic acid 1:1 (DES2), choline chloride + tartaric acid 2:1 (DES3), and choline chloride + citric acid 1:1 (DES4). It may be noted that all applied DESs fully extracts silicon and zinc (see table 1 and figure 1), high recovery levels were obtained for copper, nickel, and manganese. Recovery of aluminum and titanium are relatively low.

From the practical point of view, it may be interested that extract with choline chloride + tartaric acid is enriched with such microelements as boron, magnesium, and phosphorus, but poor in potassium and calcium in compare with other DESs. High recoveries of iron, copper, zinc, and nickel may be interesting for developments in the phytomining field.
Table 1. The content of metals in plant material \( (w_0) \), recovery of metals to various extractants: DES1 is choline chloride + malonic acid, DES2 is choline chloride + malic acid, DES3 is choline chloride + tartaric acid, DES4 is choline chloride + citric acid. All DESs with 30 wt.% water addition.

| Element | \( w_0 \), ppm | Recovery (%) |
|---------|----------------|--------------|
|         | DES1 | DES2 | DES3 | DES4 |
| B       | 14.0 | 80.2 | 78.9 | 87.2 | 39.2 |
| Mg      | 968.7| 66.4 | 63.0 | 96.8 | 72.2 |
| Al      | 380.0| 43.2 | 30.4 | 33.2 | 31.0 |
| Si      | 436.4| 100.0| 100.0| 100.0| 100.0|
| P       | 2132 | 35.2 | 32.3 | 42.3 | 38.9 |
| K       | 7548 | 65.0 | 64.8 | 29.6 | 65.6 |
| Ca      | 6790 | 70.1 | 53.0 | 24.6 | 43.2 |
| Ti      | 11.5 | 20.1 | 30.5 | 17.0 | 44.3 |
| Mn      | 140.5| 71.4 | 67.7 | 72.6 | 69.3 |
| Fe      | 102.1| 100.0| 82.1 | 80.3 | 58.6 |
| Ni      | 4.05 | 100.0| 86.2 | 79.4 | 100.0|
| Cu      | 5.64 | 94.8 | 86.8 | 100.0| 100.0|
| Zn      | 18.6 | 100.0| 100.0| 100.0| 100.0|
| Rb      | 37.5 | 65.5 | 66.3 | 46.3 | 65.0 |
| Sr      | 92.4 | 67.4 | 66.4 | 49.9 | 65.7 |
| Ba      | 73.0 | 34.2 | 56.6 | 57.9 | 50.8 |

Figure 1. The recovery of some metals from Empetrum nigrum L. DES1 is choline chloride + malonic acid, DES2 is choline chloride + malic acid, DES3 is choline chloride + tartaric acid, DES4 is choline chloride + citric acid. All DESs with 30 wt.% water addition.
4. Conclusions
The data about some elements contained in Empetrum nigrum L. and its extracts with acid-based DES were obtained in this work. It is demonstrated that the highest recoveries are for silicon, zinc, copper, nickel, and manganese. This data may be useful for the further application of DESs in the cosmetic, pharmaceutical industries and phytomining development.

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