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Kinetic modeling of the ultrasound-assisted extraction of polyphenols from *Picea abies* bark

Liliana Lazar [a], Adina Iulia Talmaciu [b], Irina Volf [c,*], Valentin I. Popa [b]

[a] "Gheorghe Asachi" Technical University of Iasi, Department of Chemical Engineering, 73 Dimitrie Mangeron Street, Iasi 700050, Romania
[b] Gheorghe Asachi" Technical University of Iasi, Department of Natural and Synthetic Polymers, 73 Dimitrie Mangeron Street, Iasi 700050, Romania
[c] "Gheorghe Asachi" Technical University of Iasi, Department of Environmental Engineering and Management, 73 Dimitrie Mangeron Street, Iasi 700050, Romania

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ABSTRACT

In this paper, the kinetics of polyphenols extraction from spruce bark (*Picea abies*) under ultrasounds action was investigated. Studies were performed in order to express the effect of some specific parameters (as: ultrasounds, surface contact between solvent and solid, extraction time and temperature) on the total phenolic content (TPC). Experiments were performed in the presence and absence of ultrasounds, using different contact surfaces between solvent and solid, for times from 5 to 75 min and temperatures of 318, 323 and 333 K. All these factors have a positive influence on the process, enhancing the extraction rate by recovering higher amounts of polyphenols. The process takes place in two stages: a fast one in the first 20–30 min (first stage), followed by a slow one approaching to an equilibrium concentration after 40 min (second stage). In these conditions, the second-order kinetic model was successfully developed for describing the mechanism of ultrasound-assisted extraction of polyphenols from *P. abies* bark. Based on this model, values of second-order extraction rate constant (k), initial extraction rate (h), saturation concentration (C_s) and activation energy (E_a) could be predicted. Model validation was done by plotting experimental and predicted values of TPC's, revealing a very good correlation between the obtained data ($R^2 > 0.98$).

1. Introduction

The interest in extraction of bioactive compounds from biomass, especially polyphenols, recently increased, as a result of the valuable biological properties exhibited by these compounds, being a great natural source of antioxidants and bio-based products such as food additives, cosmetics and pharmaceuticals (drugs and supplements).

Polyphenols represent the main group of secondary metabolites in plants, including trees, with a varied concentration, a larger amount being found in bark, roots, knots and heartwood [1]. Among all of the many species of spruce, *Picea abies* variety is characteristic to the Carpathian area (Romania). Spruce wood is manly used in wood and pulp industries, while bark is an important source of tannins, resins and volatile oils used in chemical, leathering, cosmetics and/or pharmaceuticals industries. At present in spite of its valuable chemical composition, the bark is mainly used as fuel.

The present paper offers a suitable possibility for spruce bark valorisation at industrial scale through its conversion in value added bioactive compounds for pharmaceutical, food or agriculture applications. The extraction of polyphenolic compounds from spruce bark presents many economic and environmental benefits, since the raw material comes as large amounts of industrial waste and its valorisation is achieved in accordance with the environmental sustainability principles. In this perspective, the extraction process, which has been widely studied by our research group, is aimed at separating, isolating and characterizing the polyphenols through different techniques and finding the optimum conditions of the process [2,3]. The bioactive properties of spruce bark extracts and the possibilities of valorise them in innovative applications were also investigated and reviewed previous [4].

Current research interest is focused on studying the opportunities of applying the ultrasound-assisted extraction (UAE) to obtain a large range of phytochemicals, with large applicability. Many applications of UAE are reported, especially concerning the recovery of bioactive compounds from different types of biomass at lab or industrial level, including essential oils extraction from olives [5], phenolics from apples pomace, orange peels, arecanut etc. [6–8], polysaccharides from fungus [9] or pigments from algae [10]. This method is considered one of the green extraction techniques, alongside the microwave-assisted extraction (MAE) and

* Corresponding author.
E-mail address: iwolf@tuiasi.ro (I. Volf).

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supercritical fluid extraction (SFE), given the relatively short extraction times, the decreased energy and solvent consumption and the higher yields achieved [11]. The advantage of higher yields of the target compounds can be attributed to the cavitation process that occurs during sonication, which causes ruptures in plant material cell walls, enhancing the mass transfer of the extractives in the solvent. Also, the energy consumption of UAE can be effectively decreased by employing a lower processing temperature and a shorter extraction time. A detailed analysis of UAE regarding the extraction mechanisms and process development, factors that have an influence on UAE, optimum operation conditions for polyphenols extraction using ultrasounds, and drawbacks and advantages of this technique in comparison to MAE and SFE, are synthesized in previous study [12].

In the UAE processes, the ultrasounds energy can be achieved in two ways, using either an ultrasonic bath or an ultrasonic horn (ultrasonic probe – US probe). Both systems are commercially available and largely used for bioactive compounds extraction from biomass. US probe systems are recommended as more efficient, considering that the direct contact of the transducer with the sample and the solvent can enhance the extraction efficiency, minimizing at the same time the acoustic energy losses, the biggest disadvantage of the US bath equipment. In addition, these extraction systems use high-intensity ultrasounds that can suddenly raise the medium temperature (over 358 K) and degrade the thermosensitive compounds [11]. So, the biggest advantage of the US bath systems is that the transducers are not in direct contact with the sample and even if a part of the acoustic energy is lost through the vessel and surroundings, the intensity level is lower, preventing in this way the degradation of the compounds. Comparing the ultrasonic mode of action on extraction of antioxidants from different plants, Bajerová et al. [13] reported that higher extraction levels could be achieved when using the US probe system comparing with the bath system. On the contrary, Adam's et al. [14] study shows that better recovery yields of antioxidants were obtained using a US bath instead of a US probe. It could be possible that the use of ultrasonic probe systems is a better option than the ultrasonic baths, but their efficiency largely depend on the plant material subjected to the extraction and characteristics of the target compounds.

The extraction efficiency and purity of the final recovered compounds are closely related to the process operating parameters, these factors having as well a high influence on its kinetics. For the kinetic investigation of an extraction process and in order to describe the mechanisms that drive them, experimental data are generally processed and analyzed using physical and empirical kinetic models, similarly to the solid–liquid processes [15]. Using these kinetic models, the extraction rate and stationary times required to complete the extraction process involving ultrasounds could be predicted, extremely useful data when upscaling is desired.

In recent years many kinetic studies were carried out in order to describe the ultrasound-assisted extraction process of bioactive compounds from biomass and to achieve the technological transfer from lab to pilot and even industrial scale [16–19]. Also, kinetics of UAE were studied showing that most often this process occurs following the mechanism described by the second-order kinetic model [20–22].

However, in literature there are still insufficient data on modeling and simulation of solid–liquid extraction of total phenolic compounds from biomass, especially from spruce bark, the lack of information in this field having been also remarked by others researchers [23].

The present paper deals with experimental investigation of polyphenols ultrasound-assisted extraction from bark of *P. abies*. The main goal is to evaluate kinetic models that could be applied in order to assess optimum performance of the extraction process. The variation in time of TPC, expressed as mg gallic acid equivalents (GAE) per g of bark, in presence and absence of ultrasounds, as well as the contact surface exposed to ultrasounds and extraction temperature were studied for this purpose.

2. Materials and methods

2.1. Plant material

P. abies bark was obtained as waste from a wood processing company, Romania. Before extraction, bark was dried at room temperature (291–293 K), under normal aeration conditions, up to 10.44 ± 0.18% moisture content. After drying, the spruce bark was crushed in a GrindoMix GM 2000 mill and passed through five successive sieves (by 0.25–1.25 mm diameters), for the particle size (d) distribution characterization. For all experiments, the bark was used as a mixture of: 55% particles with a size between 0.25 and 1 mm, 30% particles of size greater than 0.25 mm and 15% particles of size between 1 and 2 mm.

2.2. Extraction process

For polyphenols extraction, a mixture of ethanol–water 70% (v/v) was used. Ethanol 96% (provided by Sigma Aldrich) and distilled water (lab made using a standard GFL 2004 distillation system) were mixed to obtain the extraction solvent.

For the experiments 5 g of grinded spruce bark and 50 mL ethanol–water (70% v/v) solution were mixed into 250 mL reaction vessels in a solid/liquid (S/L) ratio equal to 1:10 g sample mL^{-1} solvent, for a quick and complete moistening of the spruce bark [34]. In the following step, the reaction vessels were placed in an ultrasonic thermostatic bath Sonorex RK 100H (by Bandelin Electronic GmbH & Co. KG, Berlin, Germany), with a frequency of 35 kHz and power of 320 W.

The extraction process was performed at three constant temperatures (318, 323, and 333 K), for different exposure times (5, 10, 20, 30, 45, 60 and 75 min). In parallel, also extractions in ultrasounds absence were performed, following the same procedure for a temperature of 323 K, in order to evaluate their influence on polyphenols extraction. Afterwards, the extracts were centrifuged using a Hettich Rotofix 32 centrifuge (at 4000 rpm for 4 min), the supernatant being carefully collected and used for further analyses.

The specific reagents for chemical analysis (Folin–Ciocalteu reagent, sodium carbonate, methanol and standards) have been provided by Sigma–Aldrich and Fluka companies.

2.3. Determination of total phenolic content (TPC)

TPC was determined using the Folin–Ciocalteu method, based on the colorimetric reaction of the sample with the Folin–Ciocalteu reagent. For all analyses 1 mL of extract was mixed with 0.5 mL Folin–Ciocalteu reagent, 2 mL Na_2CO_3 (100 g L^{-1}) and 5 mL of distilled water, and kept in dark at room temperature for 90 min. TPC, expressed as mg gallic acid equivalents per grams of spruce bark (mg GAE g^{-1}) was determined from the absorbance measured by an UV–vis spectrophotometer (GBS Avanta) at 765 nm wavelengths, taking into account the calibration curve using Gallic acid standard solution.

2.4. Extract characterization using high performance liquid chromatography (HPLC)

Prior to HPLC analysis, extracts were fractionated by liquid–liquid extraction using ethyl acetate and a separation funnel. The ethyl acetate was removed from the samples by evaporation under a vacuum pressure of 230 bar for 20 min, using a rota evaporator