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Valorization of industrial wastes from French maritime pine bark by solvent free microwave extraction of volatiles

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A B S T R A C T

Solvent Free Microwave Extraction (SFME) of oil from French maritime pine bark waste and its antioxidant activity were investigated and compared to classical hydrodistillation (HD) method (Clevenger apparatus). A central composite design combined with response surface methodology was applied to evaluate the simultaneous influences of irradiation power and irradiation time. A maximal extraction yield of 3.48% (g/100 g dry bark) was achieved under optimal extraction time of 92.4 min and an irradiation power of 803.5 W compared 2.2% obtained for the conventional method (HD). Gas chromatography coupled to mass spectrometry (GC–MS) analysis showed that SFME extract is richer in oxygenated compounds (~40%) compared to HD extract with 26%. The results also showed that the two independent variables had a statistical significant effect on the considered responses namely oil yield, total phenolic compounds (TPC) and antioxidant activity assessed by 2,2-diphenyl-1-picrylhdrazyl (DPPH). Under optimized conditions, the amount of TPC was 139.15 mg GAE/g extract largely higher than that obtained for HD extraction (14.28 15 mg GAE/g extract) suggesting that SFME represents an interesting alternative technology for production of recoverable oil from waste of French Maritime pine bark. The percentage inhibition was also higher for SFME extraction technique (71.91%) than for HD (56.51%) indicating a higher antioxidant activity.

1. Introduction

The lignocellulosic waste materials represent an interesting source of chemicals. Their abundant and renewable origin as well as the qualities found in their components converts them in a promising alternative resource. Maritime pine (*Pinus pinaster*) is a conifer native to South-Western Europe and North-Western Africa, with major forests development on Atlantic coast of southern France, Spain and Portugal (Seabra et al., 2012). Extracts isolated from plants such as pines are used as fragrances in cosmetics, flavouring additives of foods and beverages, and scenting agents in a variety of household products including detergents, soaps or insect repellent. They are also used as intermediate in the synthesis of perfume chemicals and for unconventional medicinal purposes as well as in aromatherapy (Maimoonaa et al., 2011). In this field, the traditional synthetic antioxidants food additives such as butylated hydroxyanisole (BHA) and butylated hydroxytoluene (BHT) showed some negative side effects on health (Sarikurkcu et al., 2007) due to their instability and high volatility (Li et al., 2008). Therefore, increasing interest in natural antioxidant present in the diet has developed among consumers and the scientist community an interest to replace synthetic antioxidants (Inan et al., 2012). A lot of research work have been reported about antioxidant properties of different plant extracts (Ozkan and Erdogan, 2011; Zhang et al., 2014), and confirmed that the phenolic components in isolated oils were the main source of antioxidant activity (Karabegović et al., 2014).

The technologies used to extract essential oils from plant materials are enormous and usually have some disadvantages as high temperature, long processing time as in the conventional hydrodistillation or the solvent extraction in which a loss of volatile compounds occurs during solvent removal (Rodríguez-Rojo et al., 2012). For a few years, the change in attitude has evolved increasingly to a "green" tendency and there has been an increasing demand for new cleaner techniques for essential oil extraction. These new green processes will be more environmentally friendly

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with a shorter extraction times, lesser consumption of organic solvent and energy, and minor waste and CO_2 emissions, while maintaining a high quality of extract. Some intensified extraction methods were investigated including microwave (Gholivand et al., 2013; Fernández-Agulló et al., 2015) supercritical fluids (Herzi et al., 2013; Stashenko et al., 2013), D.I.C-assisted extraction (Mellouk et al., 2013; Rezzoug, 2009) or ultrasound assisted extraction (Meullemiestre et al., 2014; González-Centeno et al., 2015; Ghitescu et al., 2015). Currently, application of microwave technology-based methods such as solvent free microwave extraction (SFME) becomes highly desirable as a valid alternative to conventional methods and this extraction technology was the subject of several studies (Chen et al., 2011; Ma et al., 2012; Ranic et al., 2014). To the best of our knowledge, no work has been published on the antioxidant activity of oil extracted from industrial wood wastes by solvent free microwave extraction. In the present work, isolation of waste extracts from French maritime pin bark issued from timber industry was optimized using SFME method. A central composite design (CCD) has been developed to assess the effect of two independent variables namely microwave irradiation power and irradiation time on extraction yield, on the amount of total phenolic compounds and on the percentage inhibition of DPPH radical (2,2-diphenyl-1-picrylhydrazyl). The results were compared with those of hydrodistillation (HD) as a conventional extraction method.

2. Materials and methods

2.1. Plant material and chemicals

French maritime pine bark (*P. pinaster*) provided by Archimbaud Company (Secondigné/Belle, France) in March 2014. The chips were coarsely crushed and dried for 24 h at 25 °C. Moisture content was measured using a halogen Moisture Analyzer (Ohaus – MB 35) at 105 °C and corresponded to 12.3% db (dry basis). After storage in a refrigerated room at 4 °C, fresh material was employed in all experiments after adding water to reach about 50% moisture content (for SFME). 2,2-Diphenyl-1-picrylhydrazyl hydrate (DPPH), anhydrous sodium carbonate, gallic acid, Folin–Ciocalteu's phenol reagent were purchased from Sigma–Aldrich and Methanol, Na_2CO_3 were from Fisher scientific.

2.2. Protocol

In the present study, the experimental design was achieved as illustrated in Fig. 1. Extraction of volatile molecules was performed by HD and SFME methods. Each HD operation was performed three times in order to test reproducible. SFME treatments were analysed and optimised through statistical study. For HD and for SFME in optimised conditions, the antioxidant activity and total phenolic compounds were evaluated.

2.3. SFME apparatus and procedure

Solvent-free microwave extraction has been performed on a Milestone NEOS microwave station (NEOS microwave laboratory oven) (Fig. 2). It is a multimode microwave reactor 2.45 GHz with a maximum delivered power of 1000 W variable in 10 W increments. Temperature was monitored by an external infrared sensor. In a typical procedure 100 g of moistened bark chips were subjected to microwave irradiations in oven cavity, initially at ambient temperature, during a fixed processing time. The microwave heating of the water contained inside the raw material allows releasing molecules constituting isolated oil. This oil was then driven by the generated vapour. A cooling system outside the microwave cavity permitted to condensate the distillate continuously (5 °C). Condensed water was refluxed to the extraction vessel in order to provide uniform conditions of temperature and humidity. Isolated oil was dried with anhydrous sodium sulphate and stored at 4 °C in the dark until used. Extraction yield was calculated according to eq. 1

$$\text{Extraction yield (\%)} = \left(\frac{\text{mass of extracted essential oil}}{\text{mass of dry material}}\right) \times 100 \quad (1)$$

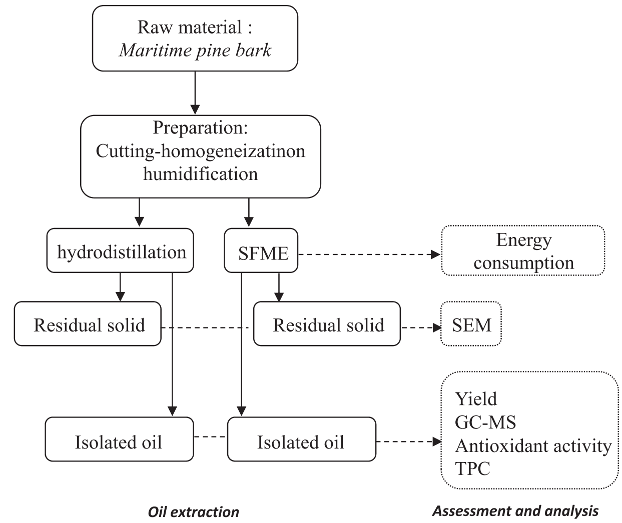

Fig. 1. Protocol of extraction and analysis of oil from maritime pine bark waste.

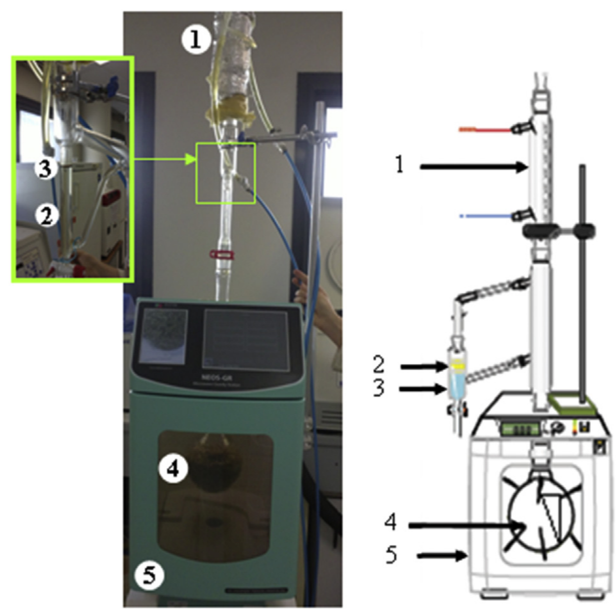

Fig. 2. Solvent free microwave extraction apparatus (SFME): (1) refrigerant system; (2) aqueous fraction; (3) oil fraction; (4) maritime pine bark; (5) microwave oven.

2.4. Hydrodistillation apparatus and procedure

Conventional hydrodistillation apparatus (Clevenger-type apparatus) according to the European Pharmacopeia (2012) was employed. A quantity of 100 g of maritime pine bark for 1 L of

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