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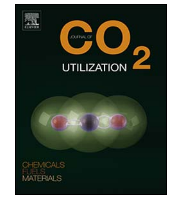

Supercritical carbon dioxide extraction of *Melaleuca cajuputi* leaves for herbicides allelopathy: Optimization and kinetics modelling

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ABSTRACT

Due to the rice production problem, control of paddy weeds with the use of allelopathy as active compounds serve as new alternative for sustainable weeds management. The volatile oil from *Melaleuca cajuputi* which has possible active allelopathy compound present is extracted and analyzed. Response Surface Methodology (RSM) with central composite rotatable design (CCRD) is used to design the experiment for optimization of supercritical carbon dioxide (SC-CO_2) extraction of volatile oil from *Melaleuca cajuputi* leaves for maximum oil yield. Three factors which included carbon dioxide (CO_2) flow rate (4–7 ml/min), temperature (40–55) and pressure (14–26 MPa) were investigated. The regression model shows a good prediction with coefficient of determination, R^2 of 0.9607. The optimum condition of SC-CO_2 extraction is determined to be at CO_2 flow rate of 5.88 ml/min, temperature of 43.10°C and pressure of 24.91 MPa with the prediction yield of 1.24 wt%. The optimum condition is validated with experimental runs which gives an average yield of 1.26 wt% which indicates good agreement between the measured and predicted value. The chemical composition of the volatile oil at optimized condition is analyzed using Gas Chromatography Mass Spectrometry (GC–MS) and Gas Chromatography with Flame Ionization Detector (GC-FID). Caryophyllene and humulene are the two major sesquiterpenes detected from the optimized condition. Thus, volatile oil extract from the foliage of *Melaleuca cajuputi* can be considered as potential source for bio-herbicides due to the presence of caryophyllene which has allelopathic effect. Kinetics studies are also studied with modified Reverchon-Sesti Osseo as the model fitting.

1. Introduction

Weeds problem has been one of the major threats that caused enormous losses in rice production with the reduction of rice yield from 44 to 96% in one crop season with uncontrolled weeds management [1]. Barnyardgrass (*Echinochloa crus-galli*) is the major notorious paddy weeds where the rice biomass is reduced by 75% and overall yield is lessen by 50% at a ratio of 100 rice plants to 10 barnyardgrass competing with each other [2]. In recent times, herbicides and other modern mode of weed control have been utilised for suppression of the emergence of paddy weeds. However, there are some challenges regarding the weeds control mentioned where conventional weeds control require more labour force and increase the cost. Similarly, the major constraints regarding the repeatable use of herbicides are herbicide-resistant weeds and health and environmental concerns [3].

Due to the pressure on importance of food security as well as rice production, implanting plants allelopathy is introduced to ensure sustainable weed management. Allelopathy is termed as interaction between plants and microorganisms by allelopathins, alleopathic and allelochemicals compounds which occurred in natural environment [4]. The capability of the allelochemical to inhibit the plant growth or seed germination is known as allelopathic potential. Due to the form of action of some allelochemicals is identical to commercialized herbicides, the use of allelopathy in weed management as bioherbicides is possible and enhanced [4]. One of the advantages of utilizing of allelochemicals is that due to its diversity, it can be targeted to specific sites in acceptor plants to kill the weeds that are already immune to the mode of action of the synthetic herbicides. Other than that, most allelopathins are totally or partially water-soluble without the need to apply together with additional surfactants [5]. Volatile oil is a potential alleopathins to be developed as bioherbicides due to the presence of terpenoids inside, especially monoterpenes and sesquiterpenes for the inhibitory action [4]. Some of examples of volatile oil that shows phytotoxic effect are from eucalyptus (*Eucalyptus*) leaves which inhibits common weeds like coffee senna (*Cassia occidentalis* L.) and barnyardgrass [6].

Melaleucae from Myrtacea family consists of 230 species internationally and it is mainly found in Austria, Indonesia, Tasmania, New Papua Guinea and south Asia in open forest and the edges of the swap

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Fig. 1. Melaleuca cajuputi leaves.

[7]. It is also well known that Melaleucae is one of the promising species in production of strong aroma volatile oil which have great economical value. *Melaleuca cajuputi*, one of the trees of current genus is renowned as the source of cajuputi oil. *Melaleuca cajuputi* has been used natively for medicinal purpose especially in Southeastern Asia [8] where it is locally named as "*Gelam*" in Malaysia. Cajuputi oil can be used as insect repellent as well as to ease headache, rheumatism and convulsions. The volatile oil from *Melaleuca cajuputi* also possesses the potential to be used as inhibitor for the growth of weeds. Nakmee et al. [9] reported that 15% leaf extract of *Melaleuca cajuputi* is effective in reducing the total weeds growth and density with the active compounds inside that give alleopathy effect is stated to be investigated further. Caryophyllene is the natural bicyclic sesquiterpenes which has anti-inflammatory, insecticidal and fungicidal activities [10] that is usually present in Melaleuca leaves that acquires the allelopathy effect. The research by Sanzhez-Munoz et al. [11] found that the caryophyllene compound affected the photosynthesis by inhibited 42% of root elongation of *Physalis ixocarpa* seedlings at 50 μg/mL and by 53% at 150 μg/mLas well as inhibited root elongation of *Echinochloa crus-galli* which is the common paddy weeds by 30%. Thus, studies are needed to determine the possible allelopathy compounds from *Melaleuca cajuputi* leaves.

There are several studies that are being conducted to extract oil from *Melaleuca cajuputi* which are maceration [9], hydrodistillation [12], soxhlet extraction as well as SC-CO_2 extraction [13]. SC-CO_2 extraction employs supercritical CO_2 to extract the active compounds from the plant matrix [14]. CO_2 serves as an ideal supercritical fluid for extraction as it is non-flammable, non-toxic and cheap and most importantly it has low supercritical temperature and pressure which are 31 °C and 7.2 MPa respectively where it undergoes supercritical state easily [15]. The supercritical CO_2 can penetrate through the solid matrix easily and diffuse the bioactive compounds and give a faster rate of extraction due to their low viscosity and relatively high diffusivity [14]. By changing the operating pressure and temperature, the density of the supercritical CO_2 can be modified which in turn controlled the solubility strength of the fluid in dissolving the bioactive compounds. Volatile oil is termed for the extracts of SC-CO_2 extraction [16] and studies have been done by Marongiu et al. [17] on SC-CO_2 extraction of volatile concentrates from myrrh and *Acorus calamus* both at 9 MPa but at temperature of 50 °C and 45 °C respectively.

In current studies, RSM is used to optimize the SC-CO_2 extraction of the *Melaleuca cajuputi* leaves to gain an insight on the effect of parameters of temperature, pressure and CO_2 flow rate on the extraction yield. RSM also helps in generating validated results with a reduced number of total run of experiment needed [18]. There are also several studies implementing RSM to optimize the operating parameters of supercritical extraction of volatile oil. For instance, Chatterjee et al. [19] had carried out optimization of 3 parameters of pressure, temperature and time of extraction to yield eugenol from tulsi leaves and reported the optimum condition at 50 °C, 20 MPa and 90 min of extraction time. Other than that, Larkeche et al. [20] had conducted the optimization research on supercritical extraction of *Juniperus communis* L. needles with 2 parameters studied which are temperature and pressure in the range of 35–55 °C and 10–30 MPa respectively. Central composite design was also utilised by Danh et al. [21] to examine the factors of pressure, temperature and time on SC-CO_2 extraction yield of volatile oil from roots of *Vetiveria zizanioides*.

In short, the primary objective of current paper is to determine the highest yield by studying the 3 parameters, CO_2 flow rate, temperature and pressure within the range of 4–7 ml/min, 40–55 °C and 14–26 MPa respectively for SC-CO_2 extraction from *Melaleuca cajuputi* leaves using RSM as design of experiment. The chemical constituents of the volatile oil from *Melaleuca cajuputi* is also compared with soxhlet extraction as well as other literature of similar plant. Modified Reverchon-Sesti Osseo model is also used for the studies of kinetics model fitting of SC-CO_2 extraction of volatile oil from *Melaleuca cajuputi*.

2. Materials and methods

2.1. Preparation of feedstock

The species used in this study was *Melaleuca cajuputi* and this species belong to Myrtacea family. The identification of the sample was verified through reference from Doran et al. [22] and Schmidt et al. [23] specifically its basic outer characteristics of 15–20 m height with narrow, thick, greenish blade size leaves. The most distinctive features of *Melaleuca cajuputi* is its white or light grey, papery, peeling bark which flaked off in large rolls. The flowers are in hairy shape of bottle-brush and its fruit is like brownish woody capsules. *Melaleuca cajuputi* leaves collected within the compound of Universiti Teknologi PETRONAS was washed with distilled water to remove the impurities. The leaves were then dried at room temperature under fan and at 50°C in the oven as in Fig. 1. The moisture content of the leaves was determined by weight loss until it is approximately 10%. Then, the leaves were grinded to the