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Comparison of kinetic models of oil extraction from sandalwood by microwave-assisted hydrodistillation

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Abstract

Sandalwood and its oil, is one of the oldest known perfume materials and has a long history (more than 4000 years) of use as mentioned in Sanskrit manuscripts. Sandalwood oil plays an important role as an export commodity in many countries and its widely used in the food, perfumery and pharmaceuticals industries. The aim of this study is to know and verify the kinetics and mechanism of microwave-assisted hydrodistillation of sandalwood based on two models. In this study, microwave-assisted hydrodistillation is used to extract essential oils from sandalwood. The extraction was carried out in ten extraction cycles of 15 min to 2.5 hours. The rate constant, the equilibrium extraction capacity, and the initial extraction rate were calculated using the two models. Kinetics of oil extraction from sandalwood by microwave-assisted hydrodistillation proved that the extraction process was based on the second-order extraction model as the experimentally done. The second-order model was satisfactorily applied, with very high coefficients of correlation (R^2 = 0.9961), showing that it perfectly described the process.

Introduction

Sandalwood and its oil, is one of the oldest known perfume materials and has a long history (more than 4000 years) of use as mentioned in Sanskrit manuscripts. Sandalwood is still used in religious rituals in India and is also used as a medium from which to carve deities and temples. The ancient Egyptians imported the wood and used it in medicine, embalming and ritual burning to venerate the gods. The oil has been in public use since the early 1800s (Arctander, 1960). Sandalwood has developed into a commercial timber crop over the past 10-15 years, with substantial sandalwood plantations established in India, China and Australia, and more modest plantings being established in Indonesia, Fiji, Vanuatu, Hawaii and Sri Lanka (Hettiarachchi *et al.,* 2010).

Sandalwood oil plays an important role as an export commodity in many countries and its widely used in the food, perfumery and pharmaceuticals industries. Sandalwood oil is used as a flavor component in many food products, including alcoholic and non-alcoholic beverages, frozen dairy desserts, candy, baked goods and gelatin and puddings at use levels generally below 0.001% (10 ppm) except in hard candy. The highest maximum use level for sandalwood oil in food products is approximately 90 ppm. Sandalwood oil is generally used as a natural flavoring substance or in conjunction with other flavor ingredients (Burdock and Carabin, 2008).

In perfumery, sandalwood oil is used extensively. It blends well with rose, violet, tuberose, clove, lavender, oakmoss and labdanum products. It is also commonly used in woody, wood-floral and Oriental-floral bases. The oil is also used as a base for co-distillation of other essential oils. It blends well with other chemicals such as ionones and methylionones. Because of the scarcity of sandalwood oil, the search for efficient synthetic substitutes has been conducted extensively to investigate the structure odor relationship of sandalwood constituents (Shvets and Dimoglo, 1998; Bajgrowicz and Frater, 2000). Several investigators have extensively studied and attempted to synthesize santalol derivatives with comparable olfactory activity (Buchbauer *et al.,* 1992; Buchbauer et al., 1997; Buchbauer et al., 2001). Opdyke (1974) reported the use of sandalwood oil in fragrances in the USA to be approximately 48,000 lb/year.

Sandalwood oil is used medicinally for common colds, bronchitis, fever, infection of the urinary tract, inflammation of the mouth and pharynx, liver and gallbladder complaints and other maladies (PDR

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Herbal, 2004). In the Indian system of medicine (Ayurvedic), sandalwood oil is largely used as a demulcent, diuretic and mild stimulant (Pande, 1977). The daily recommended dosage of sandalwood oil per the German Commission E review is 1–1.5 g for not more than six weeks (Anonymous, 1998). Imdorf et al. (1999) reported that sandalwood oil acts as a repellent of the pest Varroa jacobsoni Oud., in honey bee colonies and has been used as an acaricide. Choi *et al,*. (2006) reported modest activity against Lycoriella mali (the mushroom fly).

The main methods to obtain essential oils from the plant materials are hydrodistillation, steam distillation, solvent extraction, supercritical fluid extraction (SC-CO2) and liquid CO2 extraction have been used to obtain the volatile oil from sandalwood (Moretta *et al.,* 1998; Marongiu *et al.,* 2006). Among these method, hydrodistillation has been the most common approach to extract the essential oils from the medicine herbs and plants (Chinese Pharmacopoeia Committee, 2010). Alternative methods, employing microwaves, have been developed in order to shorten extraction time, improve the extraction yield, and reduce the operational costs. Microwave-assisted procedures for isolating essential oils have become attractive for use in laboratories and industry. The advantages of using microwave energy for oil extraction are more effective heating, fast energy transfer, faster response to process heating control, faster start-up, increased production, and elimination of some process steps.

However, to the best of authors' knowledge no work has been published on the extraction of essential oil from Santalum species using microwave ovens for heating. Therefore, the objective of this study were to investigate the potential of microwave-assisted hydrodistillation for the extraction of essential oils from sandalwood. In this study, the author also comparing the suitability of two models in order to describe the kinetics of the microwave-assisted hydrodistillation of the sandalwood. Thus the efficiency of each model was checked by comparing experimental and calculated parameters like the rate constant, the equilibrium extraction capacity, and the initial extraction rate.

Materials and Methods

Raw materials

The main raw material used in this study is sandalwood that comes from the Kupang, East Nusa Tenggara, Indonesia in powder form. All other chemicals and solvents used were of analytical grade.

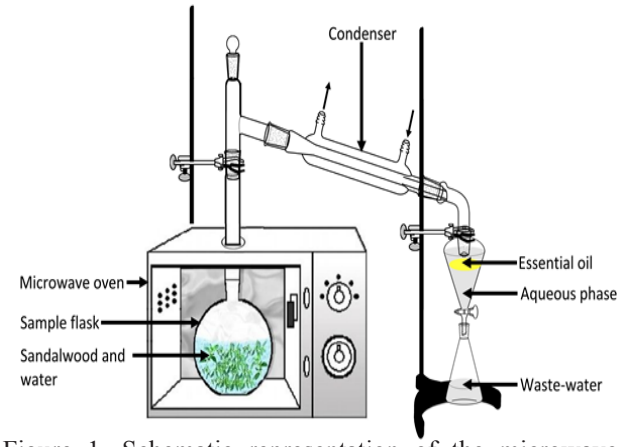

Figure 1. Schematic representation of the microwave-assisted extraction apparatus used in this study (Kusuma and Mahfud, 2016)

Microwave extraction of sandalwood oil

A domestic microwave oven (EMM-2007X, Electrolux, 20 L, 800 W; variable in 200 W increments, 2.45 GHz) was modified for microwave-assisted hydrodistillation operation. The dimensions of the PTFE-coated cavity of the microwave oven were 46.1 cm x 28.0 cm x 37.3 cm. Twenty grams of sandalwood powder samples were placed in a 1 l flask containing deionized water (400 mL). The flask was setup within the microwave oven cavity and a condenser was used on the top (outside the oven) to collect the extracted essential oils (Figure 1). The microwave oven was operated at 600 W power level for a period of 2.5 h. This period was sufficient to extract all the essential oils from the sample. The extraction was carried out in ten extraction cycles of 15 min to 2.5 hours. To remove water, the extracted essential oils were then dried over anhydrous sodium sulfate, weighed and stored in amber vials at 4 °C until they were used for analysis. The yield of sandalwood oil was found by the following equation

$$y = \frac{V}{W} \text{ X } 100 \quad (1)$$

where y is the sandalwood oil yield (%, w/w), V is the weight or mass of extracted sandalwood oil (g) and W is the weight or mass of sandalwood powder (g).

Extraction first-order model

The pseudo first-order equation of Lagergren (Lagergren, 1898; Reddad *et al.,* 2002; Ho, 2004) can be rewritten in its differential form as follows:

$$\frac{dC_t}{dt} = k_1(C_s - C_t) \quad (2)$$

where k_1 is the first-order extraction rate

constant (min-1), and t (min) the time. Equation (2) was integrated with application of the boundary conditions $C_t = 0$ at t = 0 and $C_t = C_t$ at t = t:

$$\ln\left(\frac{C_S}{C_S - C_t}\right) = k_1 t \quad (3)$$

Equation (3) may be rearranged to obtain the linear form:

$$\log(C_S - C_t) = \log(C_S) - \frac{k_1}{2.303} t \quad (4)$$

The plots of $\log(C_S - C_t)$ against t for different experimental conditions were analyzed to allow a calculation of the constant k1 from the slope and the equilibrium extraction capacity C_S (concentration obtained at saturation) from the intercept.

Extraction second-order model [Ho et al., 2005]

The second-order kinetic equation for the extraction rate can be written as follows:

$$\frac{dC_t}{dt} = k_2 (C_S - C_t)^2 \quad (5)$$

where k_2 is the second-order extraction rate constant (L g-1 min-1), CS the extraction capacity (concentration of essential oil at saturation in g L-1) and C_t is the concentration of sandalwood oil at any time t (min). By considering the initial and boundary conditions, t = 0 to t and $C_t = 0$ to C_t, the integrated rate law for a second-order extraction was obtained:

$$C_t = \frac{C_S^2 k_2 t}{1 + C_S k_2 t} \quad (6)$$

By transforming Eq. (6), a linear form shown in Eq. (7) can be obtained and the extraction rate can be written as Eq. (8):

$$\frac{t}{C_t} = \frac{1}{k_2 C_S^2} + \frac{t}{C_S} \quad (7)$$

$$\frac{C_t}{t} = \frac{1}{(1/k_2 C_S^2) + (t/C_S)} \quad (8)$$

The initial extraction rate, h, as C_t/t when t approaches 0, can be defined as:

$$h = k_2 C_S^2 \quad (9)$$

and, the concentration of essential oil at any time can be expressed after rearrangement as:

$$C_t = \frac{t}{(1/h) + (t/C_S)} \quad (10)$$

The initial extraction rate, h, the extraction capacity, C_S, and the second-order extraction rate constant, k, can be determined experimentally from the slope and intercept by plotting t/C_t versus t.

Results and Discussion

When the sandalwood was extracted with water as a solvent, the increase in concentration of the essential oil was rapid at the beginning of the process, then slowed down with time (Figure 2). The evolution of the quantity of essential oil extracted from sandalwood is displayed in the plots of concentration versus time. As shown in Figure 2, the rate of extraction was increased as the time of extraction increase until it reached plateau or constant after 120 min of extraction. 0.93% extractable oil was obtained in the 1.5 hours of extraction until it became plateau (1.02%). These experimental result were used to check two kinetic models.

According to Figure 2, the rate of extraction was fast at the beginning and slow until the end of the extraction process. The extraction process takes place in three different steps: an equilibrium phase where the phenomena of solubilization and partition intervene, in which the substrate is removed from the outer surface of the particle at an approximately constant velocity. Then, this stage is followed by an intermediary transition phase to diffusion. The resistance to mass transfer begins to appear in the solid–liquid interface; in this period the mass transfer by convection and diffusion prevails. In the last phase, the solute must overcome the interactions that bind it to the matrix and diffuse into the extracting solvent. The extraction rate in this period is low, characterized by the removal of the extract through the diffusion mechanism. This point is an irreversible step of the extraction process; it is often regarded as the limiting step of the process (Raynie, 2000). Diffusion rate decreased as the time of extraction incressed due to the high solute concentration in liquid at the third stage. Even though the extraction time incressed after the maximum sandalwood oil was extracted, it did not show any changes or significant in amount of oil extracted. The trend of sandalwood oil recovery under extraction time of 60 min (77.58%), 105 min (18.46%) and 150 min (3.96%).

Extraction first-order model

The plot of log ($C_S - C_t$) versus t (Figure 3) shows

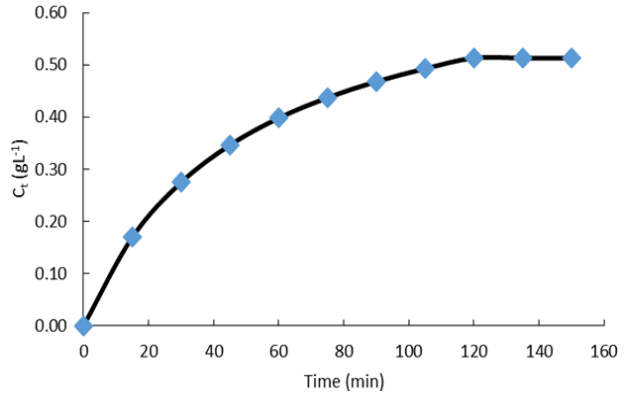

Figure 2. The concentration of sandalwood oil in the solution at any time, Ct (g L-1) versus time (min)

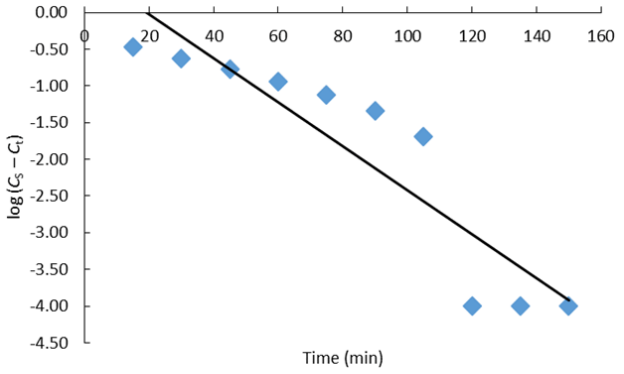

Figure 3. First-order extraction kinetics of sandalwood

Table 1. Linierization of first-order kinetic model of microwave-assisted hydrodistillation of sandalwood

C_S (g L^{-1})	k_1 (L g^{-1} min^{-1})	R^2
3.7385	0.0527	0.8281

Table 2. Linierization of second-order kinetic model of microwave-assisted hydrodistillation of sandalwood

C_S (g L^{-1})	k_2 (L g^{-1} min^{-1})	h (g L^{-1} min^{-1})	R^2
0.6797	0.0343	0.0158	0.9961

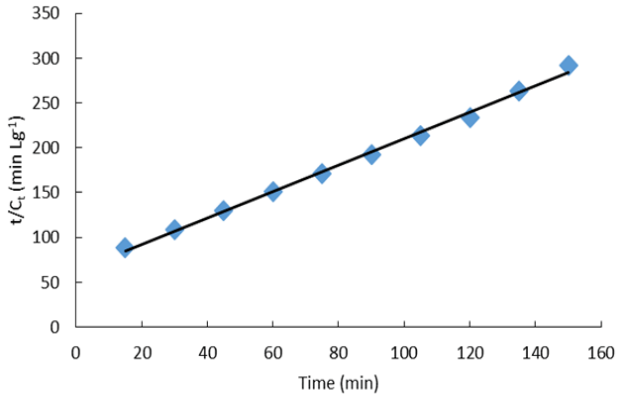

Figure 4. Second-order extraction kinetics of sandalwood

that the extraction of essential oil of sandalwood can be represented in a linear form according to the first-order model. From the slope and the intercept of the plot, k_1, C_S, and the coefficient of determination, R_2, were calculated (Table 1). These results presented generally low coefficients of determination. Furthermore, as shown in Figure 3, the linearization is better at the beginning of the process than at a later stage. Thus, the process does not globally follow the evolution of a first-order kinetic model of extraction, although the beginning of the extraction agrees with this order.

Extraction second-order model

The same data were analyzed by using a second-order kinetic model of extraction. The initial extraction rate, h, the extraction capacity, C_S, the second-order extraction rate constant, k, and coefficient of determination, R_2, were calculated experimentally by referring to the linier curve in Figure 4. From graph t/C_t versus time, slope is equal to 1/C_S, and intercept is equal to 1/h. The data showed in Table 2.

Compared with the first-order extraction model, the second-order model presents very high coefficients of determination and may be used to explain the microwave-assisted hydrodistillation process. However, two phenomena globally occur during the microwave-assisted hydrodistillation of sandalwood in which maximum extraction takes place: an intense dissolution during the initial first stage and a strong scrubbing of the most soluble molecules (normal extraction) in the second stage. The second stage is much slower because of the problems of transfer of other molecules and of the modification of the solid structure. This stage corresponds essentially to an external diffusion that concerns the soluble matter remainder.

For this study, the maximum yield oil extracted by microwave-assisted hydrodistillation is higher compared to conventional hydrodistillation. In the work of Hettiarachchi *et al.,* (2010) it was observed that sandalwood oil yield extracted by conventional hydrodistillation for 9 hours is 0.43%. The fundamentals of the microwave-assisted hydrodistillation process are different from those of conventional methods because the extraction occurs as the result of changes in the cell structure caused by electromagnetic waves. In microwave-assisted hydrodistillation, the process acceleration and high extraction yield may be the result of a synergistic combination of two transport phenomena: heat and mass gradients working in the same direction (Chemat and Cravotto, 2013). On the other hand, in conventional extractions the mass transfer occurs

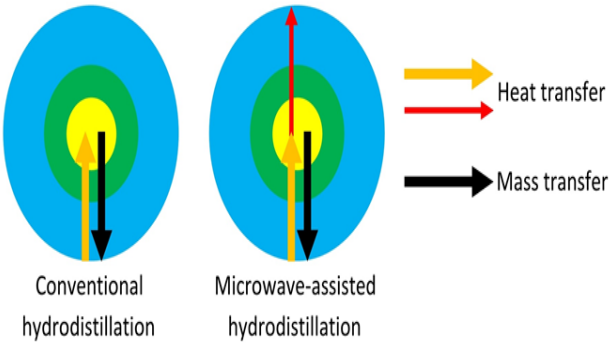

Figure 5. Heat and mass transfer mechanisms in microwave-assisted hydrodistillation and conventional hydrodistillation of sandalwood oil

from inside to the outside, although the heat transfer occurs from the outside to the inside of the substrate (Figure 5). In addition, although in conventional extraction the heat is transferred from the heating medium to the interior of the sample, in microwave-assisted hydrodistillation the heat is dissipated volumetrically inside the irradiated medium.

Conclusions

In this study, the kinetics of the microwave-assisted hydrodistillation of sandalwood was explored experimentally, and the results were checked by using two models. The established theoretical equations were used to correlate the experimental data for the kinetics of the extraction. The results allow assuming that the extraction of essential oil of sandalwood works out according to a second-order model. Compared with conventional hydrodistillation, microwave-assisted hydrodistillation for the extraction of essential oils from sandalwood is a better method. The time used in microwave-assisted hydrodistillation is much shorter than that of conventional hydrodistillation, while higher extraction yield are gotten in microwave-assisted hydrodistillation than in conventional hydrodistillation.

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