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Kinetics study of oil extraction from *Citrus auranticum* L. by solvent-free microwave extraction

Heri Septya Kusuma*, Prilia Dwi Amelia, Cininta Admiralia, Mahfud Mahfud*

Department of Chemical Engineering, Institut Teknologi Sepuluh Nopember, Jalan Raya ITS, Keputih, Sukolilo, Surabaya 60111, Indonesia

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Abstract

Citrus and its oil are of high economic and medicinal value because of their multiple uses, such as in the food industry, cosmetics and folk medicine. The aim of this study is to investigate the potential of solvent-free microwave extraction for the extraction of essential oils from *Citrus auranticum* L. peels. Specifically, this study verifies the kinetics based on second-order model and mechanism of solvent-free microwave extraction of *Citrus auranticum* L. peels. Solvent-free microwave extraction is used to extract essential oils from *Citrus auranticum* L. peels. The initial extraction rate, the extraction capacity and the second-order extraction rate constant were calculated using the model. Using a three-step experimental design of the kinetics of oil extraction from *Citrus auranticum* L. peels by solvent-free microwave extraction, this study showed that the extraction process was based on the second-order extraction model. The initial extraction rate (h), the extraction capacity (C_S), the second-order extraction rate constant (k), and coefficient of determination (R^2) was 0.7483 g L^{-1} min^{-1}, 0.7291 g L^{-1}, 1.4075 L g^{-1} min^{-1} and 0.9992, respectively.

Keywords: Citrus auranticum L.; citrus oil; kinetic study; solvent-free microwave extraction

1. Introduction

Citrus fruits and their by-products are of high economic and medicinal value because of their multiple uses, such as in the food industry, cosmetics and folk medicine [1]. In addition to large scale consumption as fresh fruits, the *Citrus* fruits are mainly processed to produce juice. The waste of *Citrus* processing industry, left after juice extraction, such as peels, seeds and pulps, corresponding to about 50% of the raw processed fruit, can be used as a potential source of valuable by-products [2]. Specifically, the *Citrus* peels, commonly treated as agro-industrial waste, are a potential source of valuable secondary plant metabolites and essential oils [3].

Citrus peel essential oils are reported to be one of the rich sources of bioactive compounds namely coumarins, flavonoids, carotenes, terpenes and linalool etc. [4]. Recently, *Citrus* peel essential oils have also been searched for their natural antioxidant and antimicrobial properties [5]. It is widely accepted that biological activities of plant materials are strongly linked with their specific chemical composition, mainly the secondary metabolites such as plant phenolics and flavonoids [6].

These substances can be extracted by different methods: hydrodistillation, extraction with organic solvent and supercritical fluid extraction (SFE) [7]. Among these methods, hydrodistillation has been the most common approach to extract the essential oils from the medicine herbs and plants [8]. 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. Novel microwave-assisted extraction (MAE) [9] methods such as microwave-assisted hydrodistillation (MAHD) [10,11,12,13] and solvent-free microwave extraction (SFME) [14] have proven to be fast and efficient methods for extracting essential oils.

However, to the best of the authors' knowledge no work has been published on the extraction of essential oil from *Citrus auranticum* L. peels using microwave ovens for heating. Therefore, the objective of this study was to investigate the potential of SFME for the extraction of essential oils from *Citrus auranticum* L. peels. In this study, the authors also attempted to know and verify the kinetics based on second-order model and mechanism of SFME of *Citrus auranticum* L. peels.

2. Materials and Methods

2.1. Raw materials

In this study, *Citrus auranticum* L. was collected from Keputran market, Surabaya, Indonesia. Orange fruits were

* Corresponding author. Tel.: +6285730780240
Email: heriseptyakusuma@gmail.com; mahfud@chem-eng.its.ac.id

peeled using a hand procedure which separates the external part of the orange, giving a yield of ±20% w/w of orange peel with respect to the whole friut. Fresh plant material was employed in solvent-free microwave extraction. All other chemicals and solvents used were of analytical grade.

2.2. Solvent-free microwave extraction

In employing SFME, we used a domestic microwave oven (EMM-2007X, Electrolux, 20 l, maximum delivered power of 800 W) with wave frequency of 2450 MHz. The dimensions of the PTFE-coated cavity of the microwave oven were 46.1 cm x 28.0 cm x 37.3 cm. The microwave oven was modified by drilling a hole at the top. A round bottom flask with a capacity of 1000 ml was placed inside the oven and was connected to the three-way adapter and liebig condenser through the hole. Then, the hole was closed with PTFE to prevent any loss of the heat inside.

In this method, fresh peels were placed in the microwave oven. Fourty grams of *Citrus auranticum* L. peels was placed inside the reaction flask and heated by microwave irradiation with 400 W (50% power) for 60 min. During the process, the vapor passed through the condenser outside the microwave cavity where it was condensed (Fig. 1). The essential oils and water was simply separated by decantation. Every 10 min, the collected essential oils was decanted from the condensate. The essential oils were collected in amber vials, dried under anhydrous sodium sulfate and stored at 4°C. The extraction yield of citrus oil was calculated according to the equation given:

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

where y is the citrus oil yield (%, w/w), V is the weight or mass of extracted citrus oil (g) and W is the weight or mass of fresh *Citrus auranticum* L. peels (g).

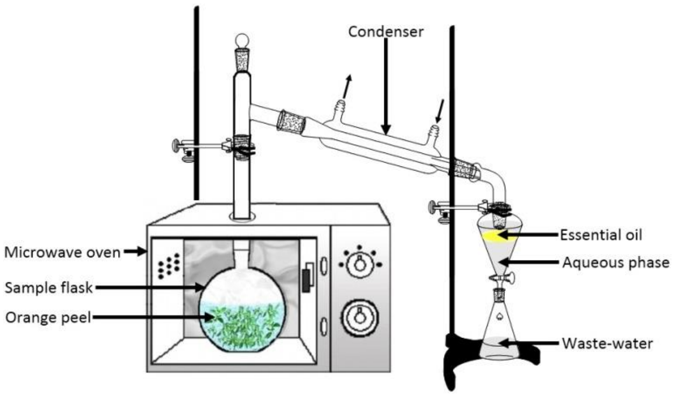

Fig. 1. Schematic representation of the solvent-free microwave extraction apparatus used in this study

2.3. Kinetic model

Second-order mechanism model means that the extraction occurs in two simultaneous processes. The amount of extracted oil increases rapidly with time at the beginning and then decreases slowly with the time until the end of extraction process [15,16,17,18]. The rate of dissolution for the essential oil contained in the solid to solution can be described by Equation (2)

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

where k is the second-order extraction rate constant (L g^{-1} min^{-1}), C_S the extraction capacity (concentration of essential oil at saturation in g L^{-1}) and C_t is the concentration of citrus 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 second-order extraction was obtained:

$$C_t = \frac{C_s^2 k\, t}{1 + C_s\, k\, t} \quad (3)$$

By transforming Eq. (3), a linear form shown in Eq. (4) can be obtained and the extraction rate can be written as Eq. (5):

$$\frac{t}{C_t} = \frac{1}{k\, C_s^2} + \frac{t}{C_s} \quad (4)$$

$$\frac{C_t}{t} = \frac{1}{1/(k\, C_s^2) + t/C_s} \quad (5)$$

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

$$h = k\, C_s^2 \quad (6)$$

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

$$C_t = \frac{t}{1/h + t/C_s} \quad (7)$$

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.

3. Results and Discussion

As shown in Fig. 2, the rate of extraction was increased as the time of extraction increased until it reached plateau or constant after 50 min of extraction. 0.65% extractable oil was obtained in the 10 min of extraction until it became plateau (0.72%). The experimental result was analyzed using second-order model by plotting t/C_t versus time as shown in Fig. 3.

According to Fig. 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 [19]. Diffusion rate decreased as the time of extraction increased due to the high solute concentration in liquid at the third stage. Even though the extraction time increased after the maximum citrus oil was extracted, it did not show any changes or significant in amount of oil extracted. The trend of citrus oil recovery under extraction time of 10 min, 50 min and 60 min, respectively was 89.89%, 9.06% and 1.05%.

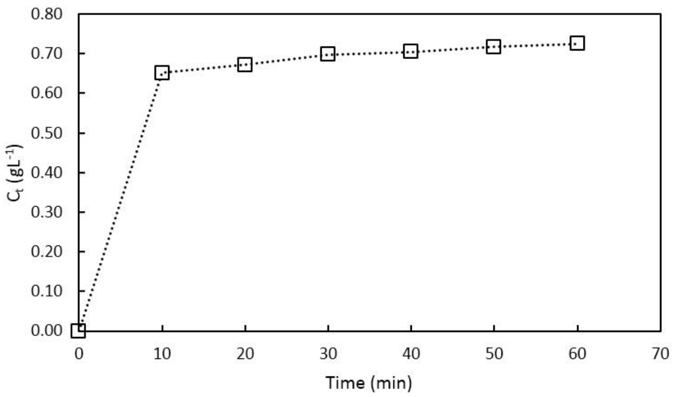

Fig. 2. The concentration of citrus oil in the solution at any time, C_t (g L^{-1}) versus time (min)

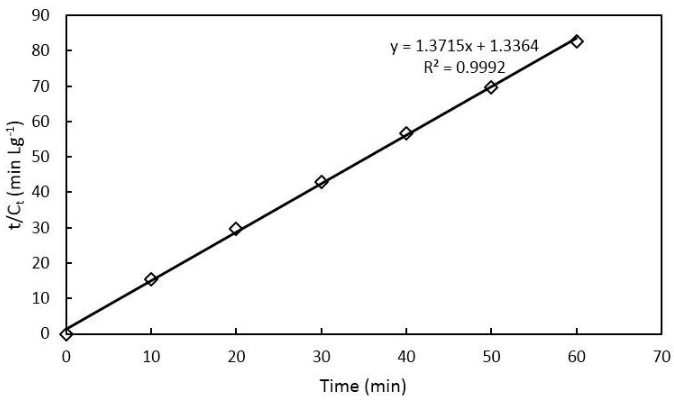

Fig. 3. Second-order extraction kinetics of citrus oil

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 Fig. 3. 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 1.

Table 1. Linierization of second-order kinetic model of solvent-free microwave extraction of *Citrus auranticum* L. peel

C_S (g L^{-1})	k (L g^{-1} min^{-1})	h (g L^{-1} min^{-1})	R^2
0.7291	1.4075	0.7483	0.9992

For this study, the maximum yield oil extracted by SFME is higher compared to conventional hydrodistillation (HD). In the work of Kamal et al. (2011) [20] it was observed that citrus oil yield extracted from fresh peels by HD for 3 hours is 0.24 ± 0.01%.

Fig. 4 shows the mechanism of SFME compared to HD method. In HD, the temperature increased often slowly, depended on the thermal conductivity and on convection currents, where the heat transfer was occurring from the outside to the inside while mass transfer was occurring from the inside to the outside of the *Citrus auranticum* L. peels [21].

Whereas, in SFME the cell was subjected to severe thermal stress, the temperature increased much faster than the conventional heating, depending on the effects of microwave irradiations and the internal dielectric heating of the *Citrus auranticum* L. peels with the action of the "in situ" water, where both the heat and mass transfers were in the same direction from the inside to the outside of the gland. As a result of internal superheating which leaded to the severe vaporization of the ''in situ" water and localized a high pressure gradient inside the gland, a dramatic expansion and a rapid rupture of the cell walls were occurring. Finally, the essential oils were migrated quickly from the inside of the *Citrus auranticum* L. peels to the surrounding.

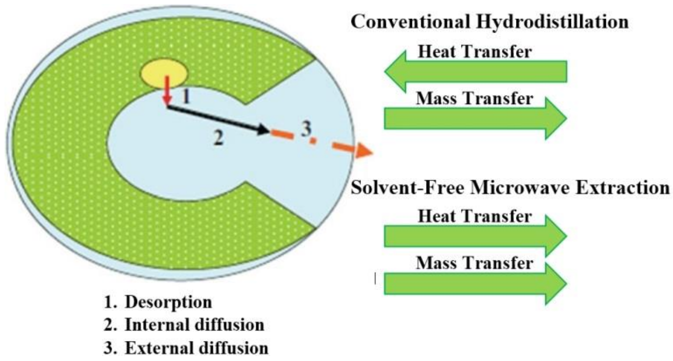

Fig. 4. Heat and mass transfer mechanisms in conventional hydrodistillation and solvent-free microwave extraction of citrus oil

4. Conclusion

The extraction yield of citrus oil obtained by SFME method for 60 min is 0.72%. Kinetics of oil extraction from *Citrus auranticum* L. peels by SFME method proved that the extraction process was based on the second-order extraction model as the experiment was conducted in three different steps. The initial extraction rate (h), the extraction capacity (C_S), the second-order extraction rate constant (k), and coefficient of determination (R^2), respectively was 0.7483 g L^{-1} min^{-1}, 0.7291 g L^{-1}, 1.4075 L g^{-1} min^{-1} and 0.9992.

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