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Mathematical models for the extraction of volatile oils and active principles from medicinal and aromatic plants. A review

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***Abstract*—Active principles cand be extracted from medicinal and aromatic plants using different methods depending on the type and condition of the plant, the active compounds to be obtained, the nature of the solvent used in the whole process (water, alcohol). State-of-the-art methods for the separation and quantification of bioactive compounds from plant materials have led to rapid and efficient development in the pharmaceutical, food and agricultural sectors. Compared to the extraction techniques in the past, it is noticed that the ones currently used are techniques with considerable selectivity and as a result, by using non-toxic solvents, they have the characteristics of ecological techniques. Recent research studies describe mathematical models that have recorded the highest extraction rate and capacity of essential oils and volatile compounds from medicinal and aromatic plants. This paper presents a review of different types of mathematical models used for the purpose of obtaining active compounds from plants in the largest possible quantity.**

Keywords—mathematical models, bioactive compounds, volatile oils, aromatic plants

I. INTRODUCTION

In the cosmetic and pharmaceutical industries, in aromatherapy, in veterinary medicine, and in agriculture, particularly through the use of volatile oils, medicinal and aromatic plants (MAP) have been employed since the dawn of humankind [1]. Modern (unconventional) extraction techniques compared to conventional extraction techniques have shorter extraction time, higher thermal decomposition and extraction selectivity and more affordable extraction solvents. The most recognized unconventional extraction techniques are: sonication extraction, steam-water distillation extraction, enzyme extraction, microwave-assisted extraction, supercritical fluid extraction, pulsed electric field extraction, pressurized liquid extraction, etc. Some of the methods listed are considered to be environmentally friendly extraction techniques because they contain lower amounts of hazardous chemicals (from the type of solvent used), allow the possibility of using renewable raw materials, construction of equipment in such a way as to prevent degradation of plant materials and the resulting compounds, and shorter extraction times so as to reduce the chances of environmental pollution with substances released during the extraction process, etc. [2].

High frequency and intense sound waves interact with plant material in the process of sonication extraction, which is a practical and accessible process [3]. The plant must be dried, ground into tiny pieces, and combined with the extraction solvent before the entire procedure can begin. The benefit of this method is that it may be used for small samples, that the extraction time and solvent consumption are decreased, and that the yield tends to be as high as possible. Because of the high energy input used in ultrasonic extraction, there is a potential of phytochemical damage [4].

Microwave-assisted extraction (MAE) is an approximately recent procedure that uses energy to heat the solvent and sample to development the rate of material transfer between dissolved substances in the sample matrix and the solvent, helping them to pass more easily into the solvent. MAE is increasingly used in the extraction of essential oils from plant materials and of the following active compounds: alkaloids,terpenes, glycosides flavones [5].

Extraction by the water-steam distillation procedure is a simple and affordable method in terms of investment [6]. The extraction process is carried out in three phases: hydrodiffusion, hydrolysis and degradation of heat unstable compounds due to high temperatures [7].

Supercritical fluid extraction can be done for both solid and liquid samples, but solids are used to a greater extent. Supercritical fluid is assigned characteristics such as density, viscosity, diffusivity, which allow it to be modified to improve transport properties [8].

Generally, a mathematical model is described as a characterization of a system that uses mathematical theories and expressions to help analyze it correctly, or to analyze the causes of certain components and generate prognostications about patterns of behavior [9]. Requirements for qualitative solvent-based extraction of active compounds from plant materials have led to advances in optimising process operating conditions (i.e. higher extraction yields) and as a result the use of mathematical models is recommended to simplify user efforts. There are a variety of mathematical models in the literature that exemplify the advantages of using a model applied to a specific procedure of extraction of active compounds from plants [10].

The purpose of this paper is to review some types of mathematical models used for the extraction of active compounds from vegetable matter, which aid in increasing extraction yields of volatile oils from medicinal and aromatic plant crops and obtaining the highest percentage of bioactive substances from plant materials.

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II. MATERIALS AND METHODS

In addition to being used to build equipment from the laboratory to the industrial scale, mathematical models can also be used to process experimental data results that are then employed in simulation processes [11].

A mathematical model should emphasize the physical processes involved in the extraction of the desired molecules, taking into account the properties of the raw materials' structural makeup as well as the outcomes of earlier experiments performed on each sample [10].

The governing equations, the defining equations, the constitutive equations, and the constraints make up the structure of a mathematical model [9].

Various models based on weight differential balance equations have been created for the supercritical liquid extraction process and are subsequently used to extract near-critical carbon dioxide raw materials [12], taking into account the geometry of the extractor, where the substances to be extracted are found in the plant, the composition of the extract, the extraction speed, the flow rate, the pressure, the temperature, and environmental conditions in the containers in which the compounds are extracted from the plant material, are all factors that are related to each other mathematically [13].

The mathematical model presented by Sovova H. virtually freely reproduces two extraction phases, the first of which is managed by stage equilibrium and the second of which is managed by internal particle diffusion. The extensive characterization of the first extraction phase, where many forms of stage equilibrium and solvent flow models will be taken into consideration, is what makes this mathematical model novel [12].

Rajesh Katiyar proposes a mathematical model established on the mass transfer-related diffusion mechanism for the water-steam distillation process [11].

III. RESULTS

A). Sovova together with his collaborators presented for the supercritical fluid extraction method a mathematical model established on the approach of ruptured and intact cells, where the model equations are used in the process of analyzing it is properties. One of the three examples described in the article is that of Reis-Vasco et al. who performed the extraction of essential oil (using supercritical fluid CO_2 at three flow rates, 100 bar of pressure, and 50 °C of temperature) from pennyroyal according to 3 different particle sizes (Fig. 1) [12].

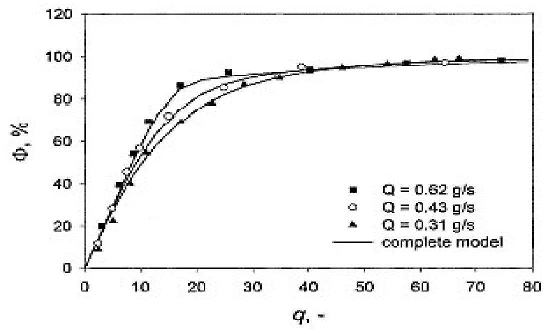

Figure 1. Extraction of pennyroyal essential oil with a 0.5 mm particle size from flowers and foliage [12]

According to Figure 1 it can be seen that when the flow rate has a value of 0.62 for contrasting fragments dimensions, the first parts of the extraction curves are of straight-line type, also called "equilibrium curves" assigned to the slant y_0=0.0015 which hold up to the yield with the value of 70%. Since the equilibrium extraction curves contain straight lines and curves it follows that they can be of two types: A and D [12].

B). Rubem M.F. Vargas and his collaborators developed in their case study a mathematical desorption model of the steam distillation extraction method of plant active compounds that has the ability to calculate volatile oil extraction curves and overall yields as a function of time [14].

The oil, obtained from the applied extraction processes, is considered as a solute for mathematical modelling and is considered to be uniformly dispersed in the solid fragments [14].

The basic active principles identified in the volatile oil of *Drimys angustifolia* Miers were as follows: rimene - 13.2%; sabinene - 11.4%; bicyclogermacene - 10.1%; myrcene - 6.5%; 1,8 cineole - 5.8%; spatulenone - 5.2%; safrole - 3.8%; terpinene-4-ol - 3.1% [14].

Equation (1) was used for the mathematical modelling [14]:

$$e(t) = \frac{M(t)}{M_\infty} = 1 - e^{-kt} \qquad (1)$$

where:

M - the maximum value of the yield in essential oil specific to each plant;

R_2 = 0.982 [14];

According to Rubem M.F.'s study, the desorption coefficient value for *Drimys angustifolia* Miers is 0.0633 min^{-1}, and the maximum oil production for this plant is also 0.3% [14].

Figure 2 compares the empirical statistics and the results of the mathematical model (specifically the yield of the steam distillation extraction method) for *D. angustifolia*, showing that this mathematical model fits the experimental data due to its ability to reproduce the extraction bends applying a single parameter that needs to be adapted as required [14].

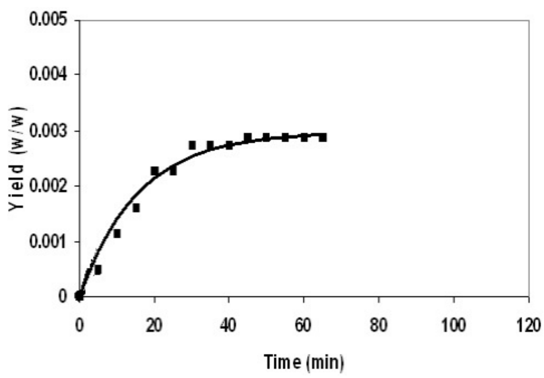

Figure 2. Time-dependent essential oil yield extraction: mathematical representation (-) and exploratory results (for *Drimys angustifolia* Miers) [14]

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C). Reverchon E. analysed the results obtained from essential oils obtained from sage by supercritical fluid extraction, through a mathematical model consisting of differential mass balances carried out throughout the extraction process [15]. Reverchon E.'s work had two main aims:

- only the extraction of sage oil without other compounds;

- to create a prototype based on the combination of divergent mass balancing.

The first attempt was to use spherical plant particles and an internal diffusion coefficient Di = $6*10^{-13}$ m^2/s (used to match the results obtained when using 0.25 mm diameter particles), but the results were not as expected. Also, the aforementioned value of D was used in the calculation of all other curves shown in Figure 3 that were obtained for fragments diameters up to 3.1 mm and resulted in a simultaneous increase in the deviation of the model curves from the experimental points and an increase in particle dimensions [15].

To obtain favourable results it was found that the ideal average thickness of sage leaves should be 0.29 mm and the same thickness was also taken into account for the height of the plate particles and the other two plate sizes should be identical to the average particle size of the load determined by the degree of grinding (at sieving) [15].

Yield curves and experimental statistics fit best at D = $6*10^{-13}$ m^2/s and particle size up to 3.10 mm (see Figure 4).

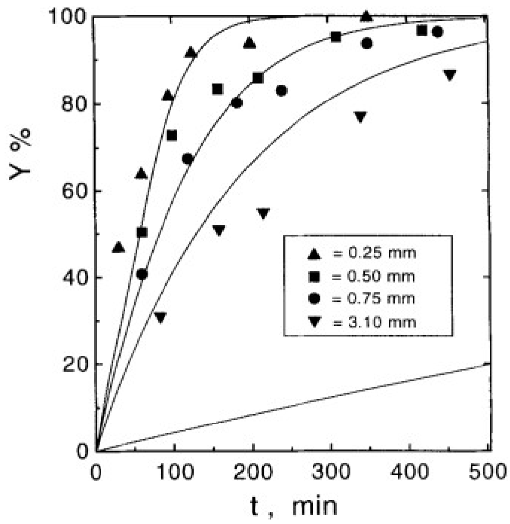

Figure 3. The first time fitting data collected using the supercritical fluid extraction method [15]

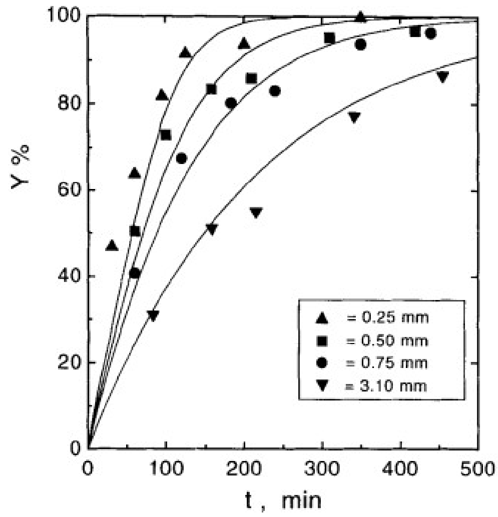

Figure 4. Supercritical fluid extraction method's best fit of the data [15]

Figures 5 and 6 illustrate the estimated solid-phase and liquid-phase volatile oil concentrations depending of time and normalized area from the bed access. It can be seen that in the liquid phase the concentration is always lower compared to the solid phase [15].

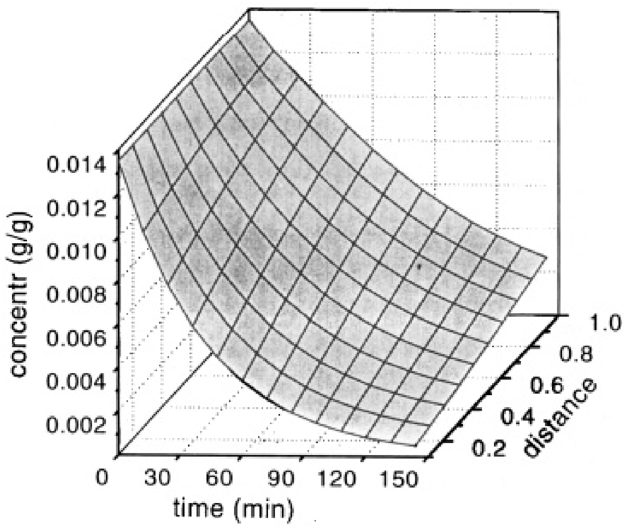

Figure 5. Calculated essential oil concentration depending of normalized area from bed access and time in the solid phase (for 0.50 mm particles) [15]

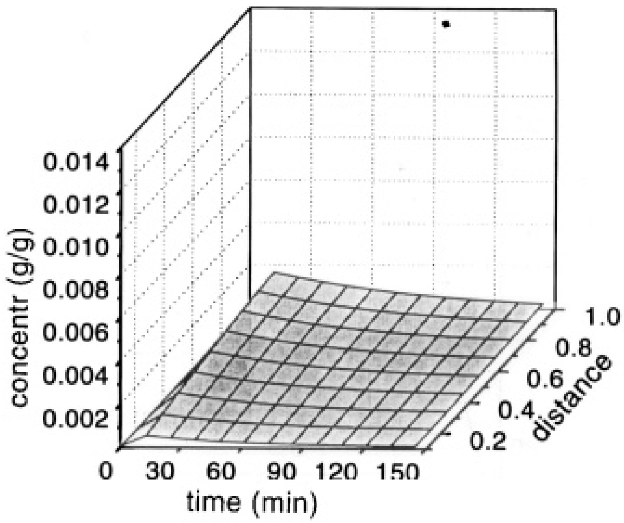

Figure 6. Essential oil concentration in the fluid phase calculated as a function of time and normalized distance from the entry to the bed (for 0.50 mm particles) [15]

D). Cristina Reche et al. proposed a mathematical model for the ultrasonic extraction method of some compounds from artichoke (*Cynara scolymus*) and extraction with mechanical agitation, comparing the results obtained at the end of the processes. This model is designed to simulate the extraction curves but also to evaluate the effects of ultrasound power density and temperature, depending on the simultaneous diffusion and convection that will be taken into account for a parametric simulation of the model [16].

The experimental part was carried out for both ultrasonic method and mechanical shaking for extraction of bioactive substances from artichoke stems that are 0.5 cm thick at the following temperatures: 25°C, 40°C, 60°C for 35 minutes. At different times during the extraction, both total chlorogenic acid content (CAC) and phenolic content (TPC) were measured and the recorded extraction yields were expressed as percentages on the graph as shown in Figure 7 [16].

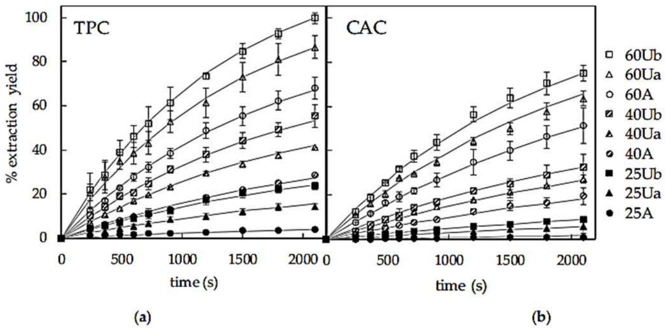

Figure 7. Chlorogenic acid (CAC) and total phenolic content (TPC) extraction curves from artichoke stem plates at 25°C, 40°C, and 60°C with stirring (A, 100 rpm), as well as acoustic aid (Ua, 200W/L, and Ub, 335 W/L) [16].

U_a - 22 mm diameter sonotrode;
U_b - 14 mm diameter sonotrode.

For 1 cm thickness of artichoke stem, temperature of 40°C and 100 rpm for mechanical stirring, respectively 200 W/L for ultrasonic extraction, new results were obtained represented in the graphs in Figure 8. For TPC, the mean relative error was about 6.7 ± 2.5% and the mean variation about 99.3 ± 0.5%, and for CAC, the mean relative error was about 5.5 ± 0.2% and the mean variation about 99.3 ± 0.1% [16].

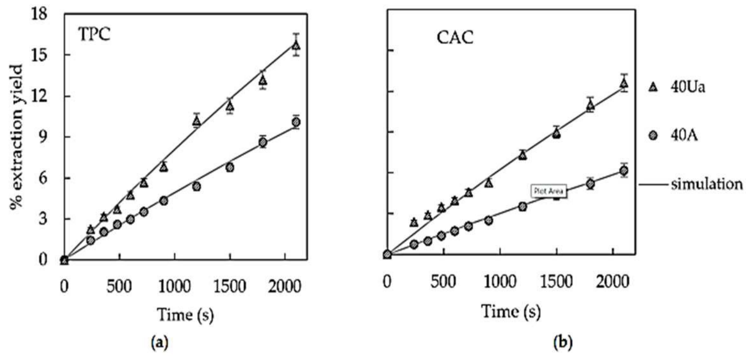

Figure 8. Chlorogenic acid (CAC) and total polyphenol content (TPC) extraction curves of artichoke stem plates (1 cm thick) at 40 °C with acoustic aid (U_a, 200 W/L) and shaking (A, 100 rpm) [16].

The experimental results show that in addition to temperature and ultrasound, the bioactive substances in artichokes increase significantly compared to classical methods of extracting active principles from plants. Even though different plant particle sizes were used, the mathematical model accurately simulated the extraction yield curves and the average relative error had a value of about 5.3% [16].

E). Patricelli's mathematical model consists of ultrasonic extraction of essential oil from *Calophyllum inophyllum* which is carried out in two stages: the fast wash stage and the slow diffusion stage. For this model, 3 parameters were analyzed: ultrasonic power, liquid-solid ratio (L/S) and extraction temperature, and the conclusions were that the oil yield showed an increase simultaneously with increasing temperature, ultrasonic power and L/S ratio [17.

Patricelli's mathematical model consists of the equation below [17]:

$$C_t = C_1(1 - \exp(-k_1 t)) + C_2(1 - \exp(-k_2 t)) \qquad (1)$$

where [17]:

- C_t - oil yield (%);
- C_1 - oil yield at equilibrium for the washing stage (%);
- C_2 - oil yield at equilibrium for the diffusion stage (%);
- k_1 - coefficient of mass transfer for the washing step (min^{-1});
- k_2 - coefficient of mass transfer for the diffusion step (min^{-1});
- t - time (min).

Figure 9 shows the experimental and simulated yields of extracted oil representative of the three distinct ultrasonic power levels [17].

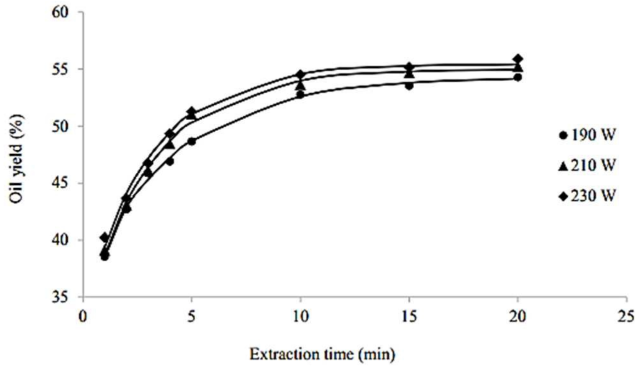

Figure 9. Impact of various ultrasonic powers on the kinetics of oil extraction from *C. inophyllum* seeds at 40°C with n-hexane as the solvent and a 20 ml/g L/S ratio [17]

According to Figure 9, in the washing phase the oil yield increased rapidly under the action of ultrasonic power (within 1-10 minutes), while in the diffusion phase (10 minutes after extraction) the oil yield increased slowly [17].

In Figure 10 the contribution of extraction temperature (between 35°C - 45°C) on oil yield was analyzed. In this case also a rapid increase was observed in the first phase after which a slow increase follows once the extraction time exceeds 10 minutes [17].

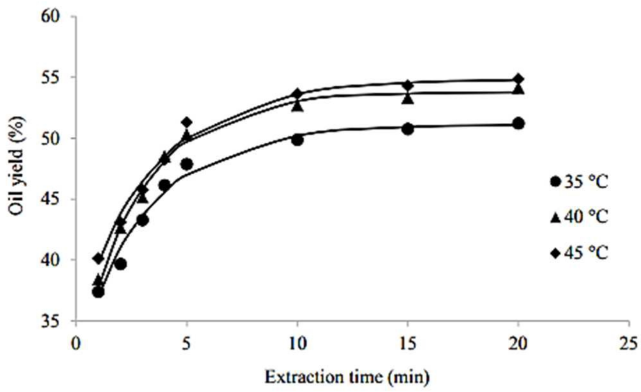

Figure 10. Effect of different extraction temperatures on the dynamics of extracting oil from C. inophyllum seeds (conditions: n-hexane as solvent, ultrasonic power 210 W, and L/S ratio 20 ml/g) [17].

According to the mathematical models discussed above, the model created by Cristina Reche et al., employed for the ultrasonic extraction process, appears to have had the maximum efficiency, with yield increases being greater as the ultrasound power density rose. When compared to the solid-liquid extraction method, temperature, in addition to the presence of ultrasound, significantly improved the value of the results.

Patricelli also developed a mathematical model for ultrasonic extraction, where the process is undertaken in two separate phases: washing and diffusion, but the largest amount of oil was extracted in the second phase of diffusion when the ultrasonic power was increased.

The other mathematical models presented for extraction methods other than sonication have several constraints in order to have the best yields in the shortest time and in the most environmentally friendly conditions, so Reverchon E.'s model for the supercritical fluid extraction method requires certain conditions for the final results to be favourable. For example, the leaf thickness of the plants should be about 0.29 mm, and for a correct graphical configuration of the curves for experimental data and yields, the particles of the plant material should be at most 3.10 mm.

IV. CONCLUSIONS

Mathematical models allow accurate simulation of extraction curves for yields of essential oil or other compounds, regardless of particle size, extraction temperatures, ultrasound power, etc.

According to the kind of extract obtained from the plant and the parameters measured during the extraction process, different types of mathematical models result even for the same type of extraction.

Mathematical models represent a good way to optimize the extraction yields of bioactive compounds from vegetable matter, to simulate and improve the extraction process of essential oils in terms of their yield, or to predict the production of essential oils depending on the process parameters analyzed for each combination in the studied range during the extraction process.

V. ACKNOWLEDGMENT

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