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Insights on the influence of microwave irradiation on the extraction of flavonoids from *Terminalia chebula*

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ABSTRACT

The aqueous extract of *Terminalia chebula* Retz. plays an important role in traditional medicinal formulations. Experiments on microwave irradiation during aqueous extraction of flavonoids from *T. chebula* reveal the influence of microwaves on solid-liquid equilibrium, leading to higher equilibrium flavonoid concentration in the liquid phase at a fixed flavonoid concentration in the solid phase. As a result, microwave assisted extraction (MAE) provided 14.17% enhancement in equilibrium yield, compared to that obtained in conventional extraction at a temperature of 100 °C and a solvent-to-feed ratio of 40 mL/g. The effective diffusion coefficient at 40 mL/g increased from 0.68×10^{-11} to 1.31×10^{-11} m^2/s due to microwave irradiation. Our data conclusively indicates that microwave assisted extraction provides higher yield, equilibrium concentration and effective diffusion coefficient. The study has also revealed the possibility of utilization of MAE for short duration extraction with lower solvent and energy consumption. The extractions were found to be endothermic and spontaneous, with the spontaneity improved due to microwave irradiation.

1. Introduction

Medicinal plants occupy an unequivocal position as the most important source of new drugs. Increased interest remains in the extraction and separation of bioactive compounds like flavonoids and other polyphenols from medicinal plants. *Terminalia chebula* Retz. (*T. chebula*) is a medicinal tree from the Combretaceae family [1], found abundantly throughout India and other parts of Southeast Asia. It is a rich source of bioactive compounds and hence is utilized in traditional medicinal systems. The dried fruit of *T. chebula* is one of the constituents of the Ayurvedic medicinal formulation *Triphala*, the other being *Terminalia bellerica* and *Phyllanthus emblica*. *T. chebula* finds therapeutic applications due to its laxative, anti-bacterial, cardiotonic, diuretic, hyperlipidemic and anti-cancer activity [2–4]. The fruits of *T. chebula* possess significant anti-fertility efficacy making it a potential herbal contraceptive [5].

Flavonoids and other polyphenolic compounds possess therapeutic applications against a wide variety of diseases caused by oxidative stress [6]. They also possess significant antioxidant activity. Flavonoids have the ability to reduce the free radical steady state concentrations in the human body [7]. They have the ability to inhibit specific enzymes and to stimulate some hormones and neurotransmitters [8].

Conventional extraction (CE) techniques like soxhlet and other related techniques have many constraints. They require a longer extraction time [9]. The prolonged extraction time in CE processes leads to loss of flavonoids due to oxidation [10]. This may be averted by making use of microwave-assisted extraction (MAE), which provides absolute superiority over the conventional extraction techniques [11,12]. The main processes occurring during microwave exposure are selective and targeted heating of materials based on their dielectric constants, followed by ionic conduction and dipole rotation of the molecules [13]. Ionic conduction is the electrophoretic migration of ions in the presence of electromagnetic field [13]. The friction produced as a result of the resistance of the solution to this migration of ions heats the solution. The alignment and re-alignment of the dipoles with an applied field is called dipole rotation [14]. The heat is produced as a result of this forced molecular randomization of the dipoles at a rate of 4.9×10^9 times per second [15].

Improved methods of extraction from natural sources are always cardinal as the extracts find significant applications in

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Nomenclature

A	surface area, m^2
Bi	Biot number
C_θ	concentration of flavonoids in solvent at time θ, mg QE mL^{-1}
C_L^*	equilibrium concentration of flavonoids in solvent, mg QE mL^{-1}
C_S	concentration of flavonoids in solid phase at time θ, mg QE/g
C_S^*	equilibrium concentration of flavonoids in solid, mg QE/g
D_a	activation energy for diffusion, kJ mol^{-1}
D_e	effective diffusion coefficient of flavonoids, m^2/s
D_p	size of particle, m
D_0	pre-exponential constant, m^2/s
E	energy consumption for microwave irradiation, kW h
E_a	activation energy for extraction, kJ mol^{-1}
h	initial extraction rate, mg QE(mL^{-1}) min^{-1}
k	extraction rate constant, (mL) mg QE^{-1} min^{-1}
k_0	temperature independent factor, (mL) mg QE^{-1} min^{-1}
K_e	extraction equilibrium constant
K_T	mass transfer coefficient, m s^{-1}
R	gas constant, J mol^{-1} K^{-1}
R_p	radius of *T. chebula* fruit particle, m
S	solvent-to-feed ratio, mL/g
T	temperature, °C or K
V_L	volume of solvent, m^3
Y_θ	total flavonoids transferred from *T. chebula* fruit at time θ, mg QE/g
Y_L^*	total flavonoids transferred from *T. chebula* fruit at equilibrium, mg QE/g
Y_{max}	total flavonoids transferred from *T. chebula* fruit determined after exhaustive extraction using multiple solvents, mg QE/g

Greek letters

θ	time, min or s
γ	Temperature extraction coefficient
ΔG°	change in Gibbs free energy, kJ mol^{-1}
ΔH°	change in enthalpy, kJ mol^{-1}
ΔS°	change in entropy, J mol^{-1} K^{-1}

perfumery, textiles, pharmaceuticals, cosmetics and food industry. MAE in its current form is a robust method, being a combination of microwave and traditional solvent extraction method. MAE was found to curtail extraction time, solvent consumption and improve the yields of solanesol from potato leaves and stems [16] and for the extraction of polyphenols from *Clinacanthus nutans* Lindau leaves and stems [17]. MAE has also been used for the extraction of various bioactive compounds like pectin from *Citrullus lanatus* fruit rinds [18], alkaloids from *Stephania sinica* [19], essential oil from oregano [20], flavonoids from cocoa leaves [21], etc.

The choice of solvent in MAE hinges on the solubility of compounds chosen for extraction and on the dielectric properties of the solvent. Most of the reported works on MAE have utilized ethanol or methanol or their aqueous solutions as the extraction solvent [22,23]. However, there are only a few reports on the use of water alone as the solvent for MAE of active principles from plants, such as those of Yang et al. [24], Wang et al. [25], Shao et al. [26] and Torun et al. [27] for extraction of compounds from *Geranium sibiricum* Linne, *Potentilla anserine* rhizomes, *Perilla frutescens* leaves and sage leaves respectively. The study of MAE of compounds from *T. chebula* using water alone as the solvent assumes importance, due to the fact that the water extract of *Triphala* is used in the preparation of *Lauha Bhasma*, a herbo-metallic drug [28] belonging to the Ayurvedic system.

Though the advantages of microwave irradiation during extraction are well realized, certain questions remain unanswered with respect to the role of microwave in the intensification of extraction. The present work aims to address the influence of microwave irradiation during extraction (microwave assisted extraction) in the context of solid-liquid equilibrium, identification of appropriate conditions for enhanced yield at short-duration microwave exposure at the lowest energy consumption and the modulation of activation energy for diffusion. For this purpose, experiments were carried out with *T. chebula* as the solid phase (feed) and water as the extraction solvent, embracing a broad array of operating conditions. The data on solid-liquid equilibrium under microwave irradiation, lowest energy consumption for short-duration extraction and the related discussions are the present work's unique contributions to literature.

2. Experimental

2.1. Materials

Dried fruits of *T. chebula* were commercially acquired, and Centre for Advanced Research in Indian System of Medicine (CARISM), SASTRA University verified the same. The fruits were milled in a blender and sieved with a rotary sieve shaker to separate particles of sizes in the range of BSS −200/+300 mesh (mean particle size – 64 μm). For the determination of total flavonoid content, aluminium nitrate and potassium acetate were procured from Hi Media Ltd., India. Flavonoid standard quercetin was acquired from Sigma-Aldrich Company, USA. DPPH for the test of antioxidant activity was purchased from SRL Chemicals, India. Solvents such as chloroform and methanol were purchased from Merck, Germany.

2.2. Extraction procedures

2.2.1. Microwave assisted extraction (MAE)

Microwave irradiation during extraction (Microwave assisted extraction – MAE) was carried out using a modified domestic microwave oven (R-219T (S)/(W), SHARP, Japan). The internal dimensions of 22-L oven were 319 mm (W) × 211 mm (H) × 336 mm (D). The outer casing of the oven was drilled for accommodating a reflux condenser on to the top and a magnetic stirrer at the bottom. The reflux condenser averted any solvent loss during microwave irradiation, and the magnetic stirrer ensured ideal mixing of the solvent and feed. The temperature control was achieved using a combination of digital temperature indicator and controller (Microsensors, India) with a 'J' type thermocouple. The duration of on-off cycles was controlled to achieve the desired temperature. An energy meter (Visiontek, India) was connected to the microwave unit and the magnetic stirrer. Hence, the energy meter readings account for total energy consumption for microwave irradiation and that for the operation of magnetic stirrer. The energy meter readings (E_T, kW h) were acquired over the entire period of MAE for all the experimental conditions. The energy consumption for the supply of microwave (E, kW h) was obtained from the difference between the energy consumption during MAE with stirring (E_T, kW h) and the energy consumption for stirring alone