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For their unconditional love, prayers and unfailing support throughout this path. Due to you, I was able to become the person I am today.

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Research article

Conventional and eco-friendly aqueous extraction methods of date palm fruit compounds: Optimization, comparison, characterization of the date pulp extract and value-added potential

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Abstract: The extraction of the total soluble solid compounds from the pulp fruit *Phoenix dactylifera* L. is a major challenge for their valorization in the date fruit industry. However, conventional aqueous extraction methods are limited in terms of efficiency and processing time. In order to optimize this process, this study explores and compares three extraction methods: microwave-assisted extraction (MAE), ultrasound-assisted extraction (UAE), and conventional water bath-assisted extraction (WAE). The primary objective of this study is to maximize extraction recovery (ER) by performing an optimization using a Box–Behnken design (BBD). The second objective is to analyze the impact of the three extraction methods on extraction recovery, functional attributes, biochemical characteristics, antioxidant and antibacterial activities of the optimized date pulp aqueous extract (DPAE). Results obtained using mathematical models showed significant differences ($p < 0.05$) between the three methods tested. Optimum extraction conditions were determined as follows: for WAE, a solid/liquid (S/L) ratio of 1/4.68 g/mL, a temperature of 80 °C,

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Abbreviations

DRDPA : Direction de la Régulation et du Développement des Productions Agricoles

AFNOR : Association Française de Normalisation

FAO: Food and Agriculture Organisation

FAOSTAT: Food and Agriculture Organization Statistics

INRAA : Institut National de la Recherche Agronomique d'Algérie

ITDAS : Institut Technique de Développement de l'Agronomie Saharienne

MADR : Ministère de l'Agriculture et du Développement Rural

DB : Degla Beida

DN : Deglet-Nour

GH : Ghars

S/L ratio: solid/liquid ratio

TNM : Total Nitrogen Matter

DE: dry extract

DW: dry weight

FW: fresh weight

GAE: gallic acid equivalent

CE: catechin equivalent

QE: quercetin equivalent

IC50: half maximal inhibitory concentration

GC-MS: gas chromatography-mass spectrometry

HPLC: chromatographie en phase liquide haute performance

eV: electron volt.

M/z: mass to charge ratio.

Exp: experimental.

Pred: predicted.

Rt: retention time.

General introduction

General introduction

The date palm (*Phoenix dactylifera* L.) is an iconic species of hot, arid regions, cultivated since prehistoric times for its nutritional and economic value, although its origins and history of exploitation remain poorly understood (Margareta et al. 2013).

Algeria is among the world's largest date producers, along with Egypt, Iran, Iraq, Saudi Arabia, and Pakistan (FAOSTAT, 2023). Between 2022 and 2023, the phoeniculture sector in Algeria recorded a moderate increase in the area under dates, rising from 175454 ha to 179150 ha, an increase of 2.11%, and production reaching 1324767.01 tonnes in 2023 compared with 1244466.87 tonnes in 2022, corresponding to growth of 6.45%, which translates into a real improvement in agricultural yield of 4.23% (FAOSTAT, 2023).

The date palm pulp is a very nutritious food. Besides the nutritional value, it is an important source of polyphenols and flavonoids and bioactive compounds which can be a source of potential nutraceutical and functional food ingredient (Alu'datt, 2025 and Maqsood et al., 2025). Due to their high content of total sugars, dates are an excellent source of energy which can reach approximately 314 kcal in 100 g of the date flesh. Glucose, fructose and sucrose are the most important carbohydrate components in date fruit (Eid et al., 2025).

The Algerian date production is divided into three categories, according to their consistency (MADR, 2021):

- The “*Deglet Nour*”, commonly known as the “noble date”, with its semi-soft consistency, mainly intended for direct consumption, accounts for 6284093 quintals, or approximately 52.86 % of the total production;
- The “*Ghars*” variety and its analogues, with a soft consistency, accounts for 2503584 quintals, or 21.06 % of the total production;
- The “*Mech Degla*” variety and its analogues, characterized by a dry consistency, and a floury texture, with a production of 3 100 353 quintals i.e. 26.08 % of the total production.

Dates with a “dry” consistency, as the “*Mech Degla*” variety, represent an abundant and accessible resource, characterized by a notable richness in sugars, phenolic compounds and dietary fiber. However, despite this interesting nutritional profile, their fibrous texture and low market attractiveness limit their integration into conventional industrial circuits, yet these fruits

harbor as yet underexploited value-added potential, particularly through their processing into high value-added products such as date powder or syrup.

The valorization of date by-products, particularly in the form of syrups, powders or bioactive extracts, thus represents a major economic and ecological opportunity. In this respect, date syrup is a priority processing option, combining tradition, naturalness and functional potential (Subhash et al., 2024). The transition towards a sustainable valuation model requires revisiting these exclusion strategies and reassessing so-called “secondary” resources (Abid & Ammar, 2022).

"*Dibs*", known since ancient times in Arab cultures, is traditionally produced by cooking and evaporating dates. It is consumed as a natural sweetener (Fattouch et al., 2016 and Alqahtani et al., 2025). However, this process remains empirical, time-consuming, energy-intensive and not very reproducible. In an industrial context, it is crucial to control, optimize and standardize syrup production, while preserving its nutritional and bioactive qualities (Mohammadi et al., 2025). In addition, consumer demand for natural, chemical additive-free products with proven health benefits is part of the growing trend towards functional foods (Süfer, 2025). Date syrup can meet these requirements, provided we improve its physicochemical quality, validate its antioxidant properties and define reliable production protocols, notably via techniques such as ultrasound and/or microwave extraction, and vacuum and/or membrane evaporation technologies (Ayour & Harrak, 2025).

In this context, the present research aims to optimize the production of a date syrup from a dry variety with low commercial value “*Mech Degla*”, by mobilizing the tools of mild thermal processes and optimization of production parameters. The experimental part of this research is part of an integrated approach to the valorization of dried dates of the “*Mech Degla*” variety, as an under-exploited resource rich in compounds of nutritional and functional interest. Using a rigorous methodological approach, it successively explores the dimensions of characterization, optimization and processing, enabling complete control of the date syrup production chain.

First, we devoted to characterizing the raw material. A morphometric and physicochemical study is carried out to identify the structural and carbohydrate parameters that define the profile of the “*Mech Degla*” date. Particular attention is paid to the quantification of total phenolic compounds, recognized for their antioxidant activity. To enhance the value of these compounds, three extraction methods are compared: conventional extraction, ultrasound-assisted extraction and microwave-assisted extraction. Optimization of operating conditions is carried out using response surface methodology, enabling the effect of parameters such as solvent type,

material/solvent ratio, irradiation power and duration to be modeled. The evaluation of extracts is completed by LC-MS/MS analysis to identify their molecular composition and *in vitro* free radical scavenging activity, helping to establish the functional value of the enriched extract.

Then, in the next chapter, continuing trend by focusing on the production of aqueous extracts from date pulp. Faced with the limitations of traditional methods, the study evaluates the effectiveness of three processes - conventional, microwave and ultrasonic - in terms of extraction yield and the quality of the extracts obtained. These extracts are then subjected to a multiparametric characterization of their physicochemical, biochemical and functional properties. Statistical modeling using the Box-Behnken design is again used to identify the interactions between factors and determine the optimum conditions for producing a quality extract.

Finally, the last chapter focuses on the final phase of transforming optimized extracts into date syrup, through a comparative kinetic study of two concentration processes: open evaporation, and vacuum-assisted evaporation. The aim is twofold: firstly, to maximize the concentration of soluble solids while preserving sensitive compounds such as phenols and reducing sugars; secondly, to assess the impact of each method on the physicochemical properties of the finished syrup. Advanced analytical tools, such as spectrophotometry, HMF assay, phenolic profiling by HPLC-UV, and sugar profiling by GC-MS enable detailed comparison of the products obtained and identification of the process best suited to guaranteeing natural, stable, antioxidant-rich syrup that meets quality standards.

The gradual combination of these three experimental aspects has enabled us to build a coherent value-adding strategy, from the initial characterization of the fruit to the production of a high value-added finished product that meets the requirements of naturalness, functionality and sustainability.

The aim of this project is to make an original contribution to the valorization of Algerian dates, through an integrated approach geared towards industrial applications. Not only does it enable us to rehabilitate a neglected local resource, it also proposes a reproducible technological model that can be adapted to other products or regions.

The expected results could thus be of interest to the agri-food processing sector, food innovation start-ups, and more broadly to sustainable development players seeking to reconcile quality, naturalness and the enhancement of local resources.

Bibliographic
Part

Chapter 1

Overview on date palm fruit (*Phoenix dactylifera* L.) and its natural date syrup

1.1. Date Palm (*Phoenix dactylifera* L.)

The date palm is native to arid areas of the Old World and gradually spread globally, first by the Arabs and then by European explorations. Cultivated both for its fruits and for ornamental purposes, it is now intensively exploited in Mediterranean Africa, the Middle East and the United States. In the regions of ancient culture, it remains mainly conducted in extensive systems or associated with other cultures, some palm groves having evolved into quasi-natural stands (Munier, 1973).

1.1.1. The date palm's economic significance

Internationally: date palm is a globally important crop. Algeria is one of the leading date producing countries, with 1.136.025 tonnes in 2019 (FAOSTAT, 2020) (Figure 1.1).

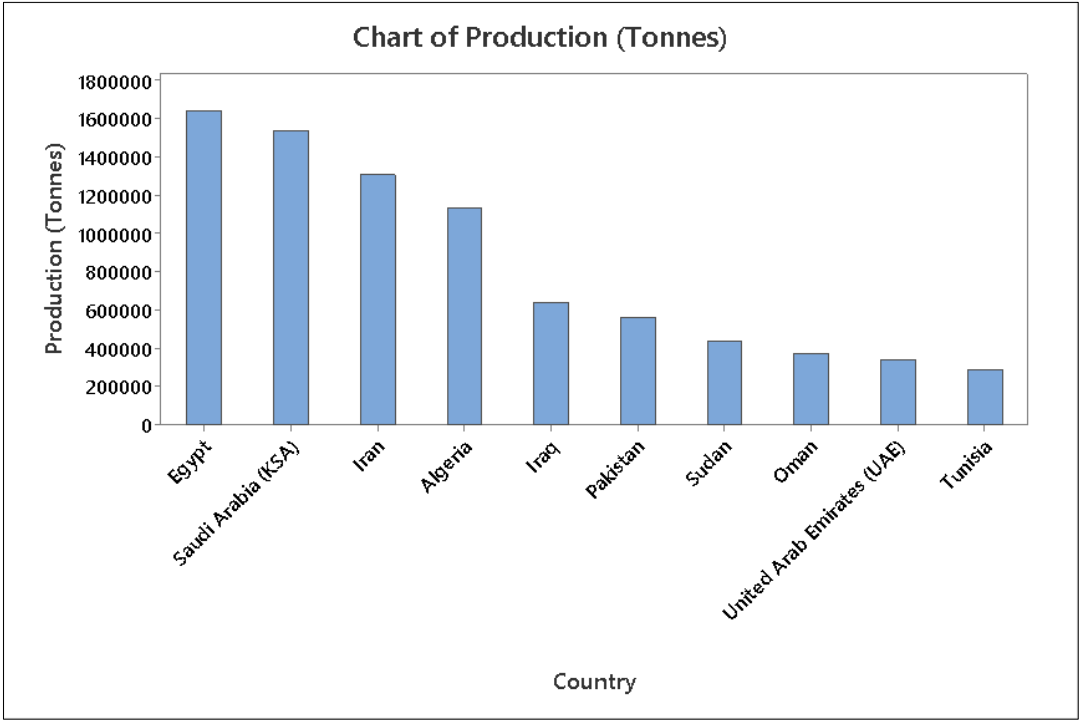


Figure 1.1. 2019 ranking of the top ten largest date producers in the world (FAOSTAT, 2020).

At the national level

- **Area, potential in palms and repARATION of the production**

Phoenician cultivation in Algeria covers an area of more than 169 786 thousand hectares, with over 19 million palm trees planted together. However, the southeast and south-central regions of the country contain the majority of these palms (MADR, 2021). As shown in figure I.2, Date palm is grown in the Saharan regions of the country: Ziban (Biskra), Le Souf (El-Oued), Oued-Righ (M'Ghaïr, Touggourt...), Ouargla, M'Zab (Ghardaïa), Touat (Adrar), Gourrara (Timimoun), Tidikelt (In-Salah), Saoura (Bechar), Hoggar-Tassili (Tamanrasset, Djanet). Small palm groves are also found in the southern steppes of the regions (Tebessa, Khenchella, Batna, Djelfa, Laghouat, M'Sila, Naâma, El-Bayedh). Furthermore, the palm tree plantations in Biskra cover a total area of 26%, whereas El-Oued has 23%, Adrar has 17%, and Ouargla has 13%. (Figure I.3).

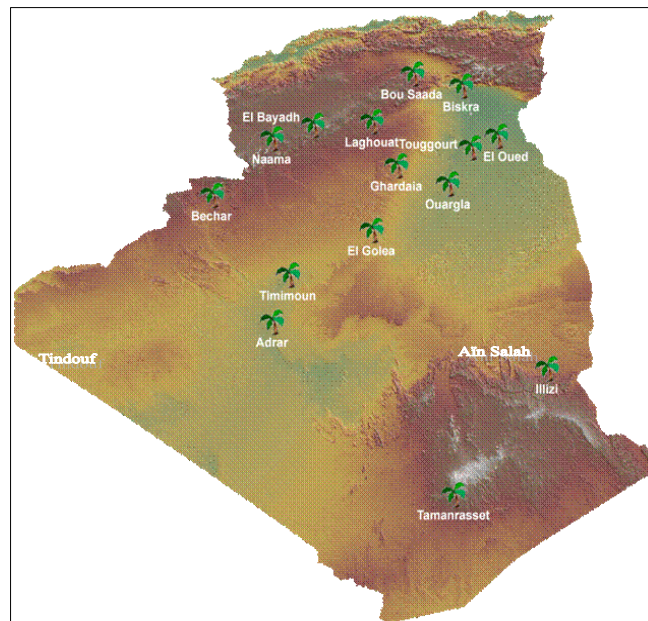


Figure I.2 : Location of oases in the Algerian Sahara

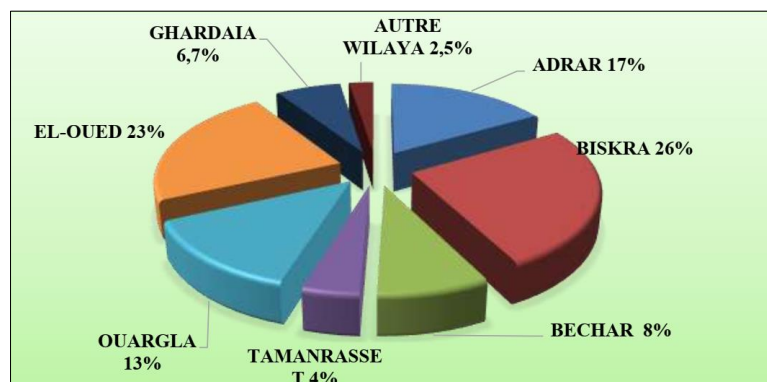


Figure I.3 : Algerian date palm distribution by region in 2019 (MADR, 2021)

National production in Algeria surpassed 12 million quintals of all cultivars in 2019, including a large volume (2 228 150 quintals), part of which is destined to agri-food processing (MADR, 2021). According to figure I.4, Biskra, Ouargla, Adrar, El Oued, Ghardaïa, and Bechar appear as the main production regions.

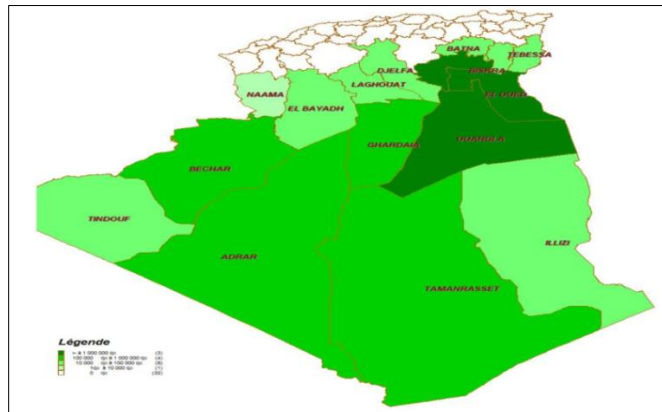


Figure 1.4 : Distribution of date's production in Algeria (MADR, 2021)

As represented by Figure (I.5 a,b), most date palms in Algeria are primarily cultivated for the *Deglet Nour* and *Degla Beida* cultivars, while a lesser number of trees are devoted to the cultivation of *Ghars*, a sort of soft dates. This distribution represents the proportional significance of these different cultivars in the cultivation and production of dates in Algeria. Analysis of these proportions can provide insights into culture and market strategies, as well as consumer and exporter preferences.

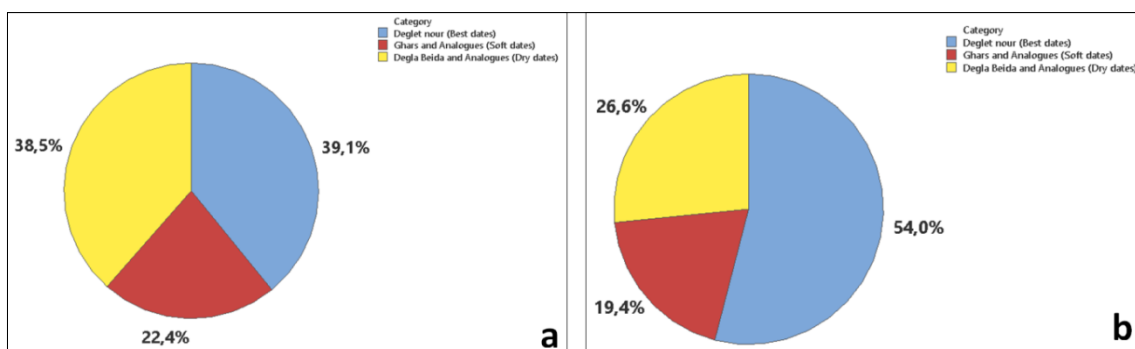


Figure 1.5 : Distribution of date palm' trees

(a) and date's production in Algeria per category of date palm fruit, and (b) (MADR, 2021)

1.1.2. Taxonomy and botanical Aspects

The tree was first described and named by Pline, an ancient savant. In 1734, Linné officially adopted the name *Phoenix dactylifera* and provided a comprehensive description of it (Gilles, 1998). The date palm plant is a monocotyledonous arborescent and diploid ($2n=36$ chromosomes).

As reported by Munier (1973), "*Phoenix dactylifera* L." is a member of the Arecaceae or Palmaceae family and is more generally known as the date palm. It has close to 14 species, 200 genera, and more than 2500 species overall. The taxonomic classification is as follows: *Phanerogames* Branch, *Angiosperms* Subbranch, *Monocotyledons* Class, *Phoenocoids* Group, *Arecaceae* Family, *Coryphoideae* Subfamily, *Phoenix* Gender, and *Dactylifera* L. Species. This plant exhibits resilience in thriving in arid and scorching climatic circumstances, while also displaying tolerance towards saline and alkaline soil types. It needs a copious supply of subterranean water sources in close proximity or the provision of irrigation. Additionally, it has the ability to thrive within a temperature range of 12.7 to 27.5°C, and can withstand temperatures as high as 50°C (Munier, 1973; Al-Yahyai & Manickavasagan, 2012). Regarding botanical description, the palm date tree is of medium size, often reaching heights of 15 to over 30 meters and having a cross-sectional diameter of 40-80 cm. It may grow individually or create a cluster with additional stems originating from a single root system (Al-Shahib & Marshall, 2003; Chao & Krueger, 2007; COAG, 2020). The leaves are 4–6 cm in length and have spines on the petiole (Figure I.6).

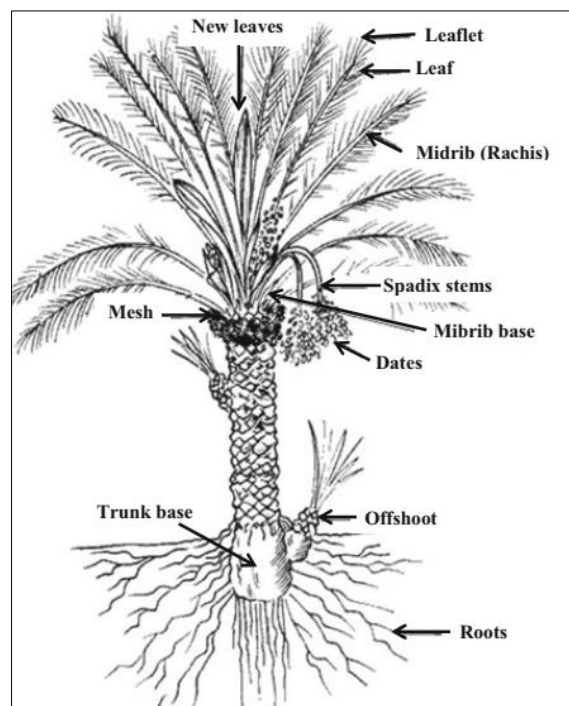


Figure 1.6 : Foliage of the date palm (Awad et al., 2020)

1.2. Date palm fruit

1.2.1. Fruit description and ripening stages

The fruit of the date palm (*Phoenix dactylifera* L.) is an elongated drupe, consists of four parts: the pericarp, the mesocarp, the endocarp, and the seed (Figure I.7).

The mesocarp, which makes up the majority of the pulp, is comprised of an outer layer and an inner layer, with tannin-rich cells acting as a barrier between them. The seed exhibits morphological variations, including differences in the depth of the ventral strain and the position of the micropyle, which are dependent on the specific cultivars (Ghnimi et al., 2017). Its attributes, such as their dimensions, form, weight, and color as well as those of the seeds, exhibit significant variation contingent upon the agro-climate conditions and cultivated cultivars. The fruits typically measures between 2 and 7 cm in length and have a range of 9.23 to 32.63 grams, and the seeds weigh between 0.96 and 1.67 grams (Belguedj et al., 2023). The color can vary from a pale yellow to a deep brown, depending on the specific variety and the level of ripeness. The fruit develops from a suspended cluster of flowers, known as an inflorescence, termed a date bunch, which can hold several dates (Fernández-López et al., 2022).

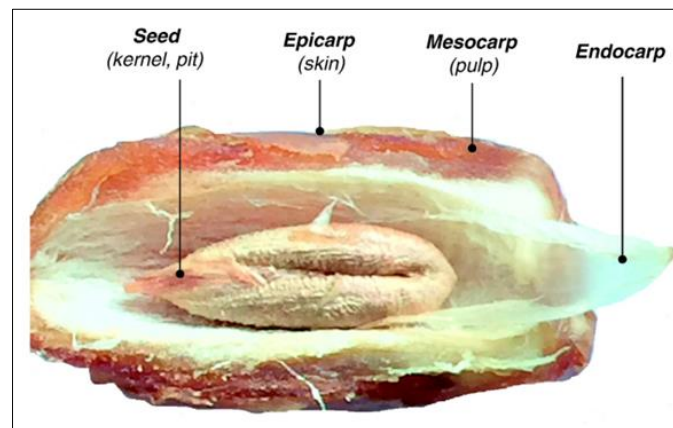


Figure 1.7: The anatomy of the date fruit at *Tamr* stage showing the epicarp, mesocarp, endocarp and seed (Ghnimi et al., 2017)

During each stage, the fruit undergoes notable variations in its texture, color, water content, and chemical composition. As reported by Bousdira (2007), the maturation stage of the date fruit is categorized into five primary stages (Figure I.8):

- A. *Khalal*: Just after fecundation. This stage leaves the date spherical, yellowish, and greenish.
- B. *Blah*: the date grows rapidly to become apple green. This stage is divided into two phases: In the 2nd phase, weight and volume increase, reducing sugars accumulate, total sugars and solid matter rise gradually but significantly, and acidity and moisture ratio rise. The second phase is characterized by slower weight and volume increase, slower decreasing sugar accumulation rate, slower total sugar formation, and somewhat lower acidity and moisture. The taste of the date at this stage is astringent and bitter (with a few exceptions) due to the presence of a high level of tannins.

- C. *Bser*: the developmental stage of the date refers to the point at which it reaches its ultimate form and size and transitions from its initial green hue to a distinct color that is unique to the specific cultivar. This color might be yellow, brown, black, or red (IPGRI, INRAs/PNUD, FEM, 2005). This stage is distinguished by a gradual increase in weight leading up to the end. There is a significant and fast increase in the formation of sucrose and total sugars, but the accumulation of reducing sugars is minimal. This stage has the highest concentration of sugar, particularly sucrose, the exponential expansion of solid materials, reduction in acidity and humidity, the flavor of the date is a combination of sweetness and bitterness, attributed to the presence of tannins.
- D. *Rutab*: the onset of ripening, this stage is characterized by the gradual appearance of softening zone. In general, according to Al-Bekr (2002), this change of texture begins with the upper part of the date (perianthe side). Then there is homogenization of color and texture. There are varieties where the softening appears randomly. The date becomes translucent; its skin changes from yellow chrome to an almost black or green brown depending on the cultivar. For dry and semi-dry dates, the date does not go through this stage, the "*Bser*" turns to brown or a reddish color, the texture is wrinkled (1/2 dry) or hard (dry). During this stage the tannins precipitate entirely, in insoluble form thus making the bitter astringent taste disappear, and the date becomes sweet. The formation of sugars very weak; however, there is an inversion of disaccharides (saccharose) into monosaccharids (glucose and fructose).
- E. *Tamr* (totally mature): the date is fully ripe. The consistency of the fruit is comparable to that of grapes and prunes. In most cultivars, the epicarp adheres to the mesocarp and scratches as it decreases in volume. The color of the epidermis and pulp gradually darkened. The fruit loses a lot of water. The sugar/water ratio remains high enough to prevent fermentation and acidification.

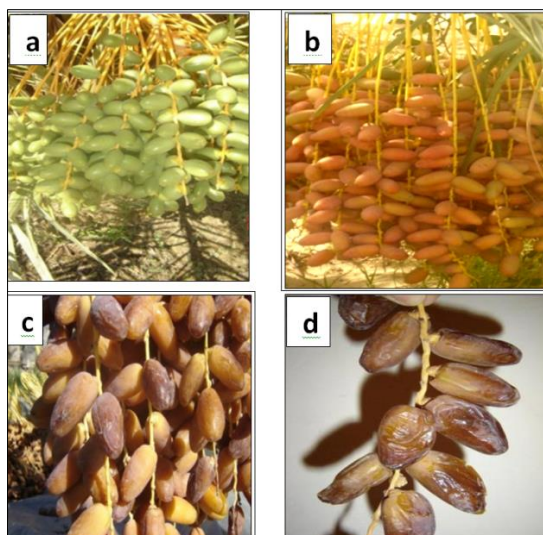


Figure 1.8 : Different ripening stages of date palm fruit a) *Khalal*, b) *Blah and Bser*, c) *Rutab*, and d) *Tamr* (Ghnimi et al., 2017)

1.2.2. Classification and cultivars

Tamr stage date fruits exhibit variations in dimension, form, colour, consistency, and flavoring, which are influenced by the specific cultivars, aside from agronomic and climatic factors. As reported by Hussein et al., (1979), the edible parts of fruits vary in consistency and are characterized by moisture content at fresh *Tamr* stage as soft ($\geq 30\%$ moisture), semi-dry (20-30% moisture), or dry ($\leq 20\%$ moisture, and < 0.65 water activity). The moisture content of the fruits, the presence of inverted sugars and possibly sucrose, allowed many authors to characterize certain cultivars of dates. Indeed, Belguedj (2002), in his project "Characteristics of date palm fruit cultivars in southeastern Algeria" resulted in the classification of the 131 dater cultivars according to moisture, reducing sugars and sucrose (Figure 1.9). This study revealed the predominance of soft and semi-soft varieties represented by 91% of the population studied. This category of date is low in sucrose (0 – 20%). Only 9% of the population represented dry varieties, i.e. cultivars high in sucrose (30 – 50%) and relatively low in reducing sugars.

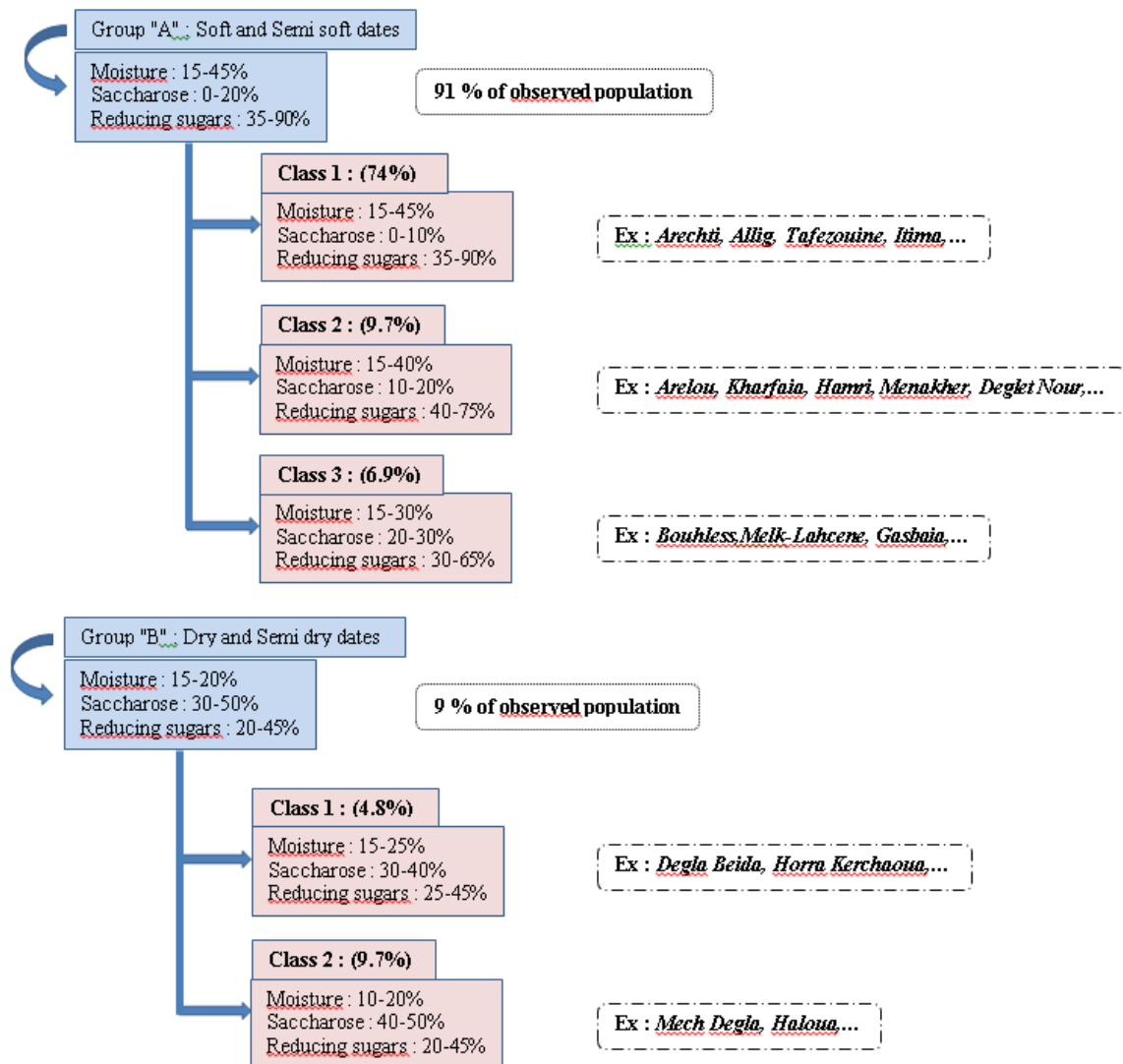


Figure 1.9 : Classification of 131 date palm fruit cultivars in southeastern Algeria (Belguedj, 2002)

1.2.3. Biochemical composition and biological activities

Estanove (1990) states that the composition of dates mostly includes moisture, sugars such as sucrose, glucose, fructose, and others, as well as non-sugars including proteins, lipids, cellulose, mineral salts, vitamins, and so on. This information is visually represented in Figure 1.10.

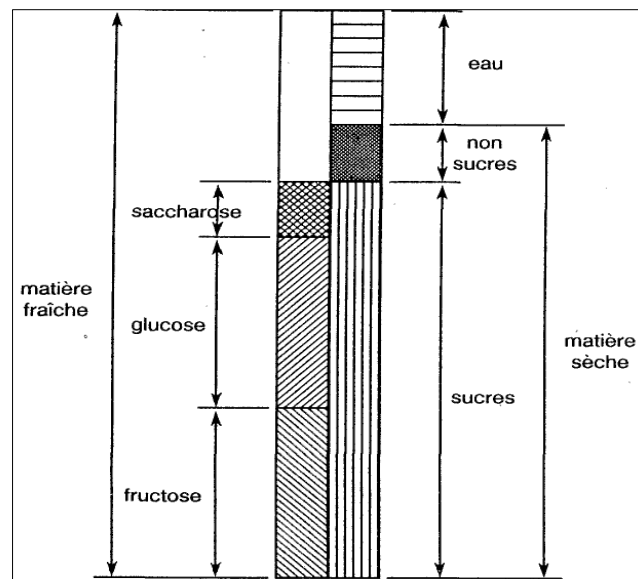


Figure 1.10: Composition of date palm fruit (Estanove, 1990)

The most significant fraction of the total solid matter is sugar, which is comprised of three main components: fructose, glucose, and sucrose. The three sugars found in dates are monosaccharids and disaccharides, and their amounts vary depending on the date variety and the stage of ripeness. Fructose and glucose, two simple sugars, appear to dominate in quantity compared to sucrose, a disaccharide. This distribution of sugars directly influences the organoleptic characteristics of dates, such as sweetness and flavor. The non-sugar fraction represents a relatively small portion of dry matter, probably comprising components such as dietary fibers, proteins, vitamins and minerals and other bioactive compounds that contribute to the overall nutritional value of dates. The biochemical composition of the date palm fruit has been studied by various researchers. This paragraph highlights on the nutritional and antioxidant components of date fruit. Dates are a high-carbohydrate fruit, with total sugar amount range from 59.6 g/100 g to 76.8 g/100 grams. This wide range of values shows that dates are a concentrated source of energy. The moisture and sugar content in date fruits have relationships, with soft date variety mostly containing reducing sugars as glucose and fructose, whereas varieties with dry consistence have a high proportion of saccharose (Ghnimi et al., 2017). The fiber content, important for digestive regulation and the prevention of metabolic diseases, ranges from 2.2 g/100 g to 9.1 g/100 grams.

Significant differences observed may have an impact on the functional properties of dates in human food. However, although present in small amounts, are essential for the amino acid intake. The protein content ranges from 2.1 g/100 g to 3.1 g/100 grams. These values indicate a modest but significant contribution to the nutritional's date value.

The fat content of date varies from 0.12 g/100 g to 7.33 g/100 grams. Such a low fat content in most samples, with the exception of one extreme case, is typical of dried fruits; making dates a low-fat option for low-calorie diets. Ashes, representing the mineral fraction of dates, range from 1.5 g/100 g to 6.2 g/100 grams. This range indicates variability in the content of essential minerals, potentially reflecting differences in growing conditions or date varieties (Habib and Ibrahim, 2011; Abdul-Hamid et al., 2020). The fruit contains 1.5–1.8 g of minerals and trace elements per 100 g. The potassium content of this fruit is around 670 mg/100 g. Calcium (62 mg), magnesium (58 mg), and iron (3 mg) are also abundant (Amellal, 2008).

Dates are a significant source of diverse bioactive compounds, namely carotenoids and phenolic compounds, such as flavanones (naringenin and epicatechin), flavonols (chrysoeriol, quercetin, rutin, iso-rhamnetin, and isoquercetin), and flavones (apigenin and luteolin), which have been identified in various varieties of date fruit (Saafi et al., 2011). The pharmacological properties of dates are thoroughly investigated for their beneficial effects on health, including anti-inflammatory, nephroprotective, hepatoprotective, gastroprotective, anti-tumor, anti-cancer, antioxidant, and anti-mutagenic activity, partly due to their rich phenolic compounds (Ben Thabet et al., 2009; Tang et al., 2013; Mahomoodally et al., 2023; and Sayas-Barberá et al., 2024).

1.2.4. Utilization of date palm fruit in food industry and date by-products

Nutritious components, including carbohydrates, dietary fiber, vitamins, amino acids, and bioactive compounds, including anthocyanins, sterols, carotenoids, and flavonoids, are abundant in date fruits. Their biochemical composition is contingent upon the variety, the growth environment, and the fruit maturation stage. The latter undergo three distinct phases (*Bser*, *Rutab*, and *Tmar*), which lead to substantial modifications in flavor, texture, color, and composition. The date by-products can be entirely converted into value-added products through the use of environmentally friendly processes. The food industry can benefit from the integration of these products, which possess specific functional characteristics. Beside food industry, dates provide a valuable resource for several industries such as cosmetics, and medicines, which helps in creating a sustainable palm date value chain using a circular economy strategy (Manai et al., 2024). Dates, when intended for direct consumption, are generally of high quality. However, date varieties with low commercial value but high nutritional and energy potential are an abundant resource that deserves to be valued through

processing. These dates can thus be used as raw material for a wide range of semi-finished products, such as date paste or pulp powder (Messadi et al., 2023 and Muñoz-Bas et al., 2024), integrated into products such as bakery, pastry and confectionery. Furthermore, through various technological processes, these dates can also be processed into high-value products such as date syrup (Julai et al., 2023), liquid sugar (Farahnaky et al., 2016), jams (Besbes et al., 2009), and marmalades (Balvardi et al., 2021). Dates can also undergo fermentation processes (Cantadori et al., 2022) to produce wine (Awe et al., 2015), vinegar (Siddeeg et al., 2019). In addition, bioprocesses may be used to transform these dates into products such as organic acids, in particular citric acid (Chergui et al., 2021), surgical ethanol (Chitranshi et al., 2021), and microbial culture media (Rini et al., 2023), production of prebiotics (FOS) (Chandrasekaran & Bahkali, 2013, Kumar et al., 2024), single-celled proteins (Shah & Hajoori, 2022), essential in the food and pharmaceutical industries.

1.3. Date syrup

Date syrup, is a widely and naturally derived date product; this syrup is valued for its nutritious benefits, abundance of antioxidants, and pleasant sweet flavor. What is the specific physico-chemical and biochemical properties of this product and what are the traditional and industrial methods used to make it? This section seeks to focus on practices in Algeria and throughout the world.

1.3.1. Origin

Date syrup, usually named traditionally as "*Dibs*" or "*Rob*", is extensively used in the regions of the North Africa and the Middle East (Barreveld, 1993).

Date syrup it is typically manufactured using two distinct methods:

- As an unintentional by-product during the storage of dates' bagged, moist dates (particularly in the Gulf region), It does not yield a maximum of 6% of the weight of the date, the quality of the syrup as such is quite good, as it is the natural direct extract of fruit, but the contamination with foreign bodies, due to the rudimentary methods of collecting the product, is quite high.
- On special occasions, such as the birthday of the commemoration of the Prophet's birthday or the birth of a child, at the household or village level by extracting and boiling down the date juice.

1.3.2. Production : From traditionnel to industriel production processus

Dates that are not appropriate for direct consumption, have a significant potential for sugar recovery, due to their low market value, since they are generally regarded as by-products or waste. This includes dry and damaged dates resulting from sorting, as well as dates that are too soft or adhesive to be suitably packed.

The date syrup industry in Algeria began through traditional cooking methods in the thirties and forties of the last century. The artisanal processing of dates in Algeria (Figure 1.11) is anchored in ancestral practices, passed on from generation to generation. Conventional methods of making date syrup in rural regions sometimes lack proper management. The use of primitive handcraft techniques often yields sub-standard syrup, distinguished by its dark color, indistinct consistency, and charred flavor. The conventional approach involves boiling a small amount of dates, filtering the mixture, and then concentrating the syrup by extended boiling. This cooking method is often performed in a basic cooking pot, which is not very effective since the date pulp takes a long time to break down without the use of a mechanical straining device. In addition, cooking the dates directly on heat without frequent stirring causes the dates in the bottom of the container to get excessively hot, leading to partial carbonization of the product. The extended heating process is the primary factor responsible for the dark color and charred flavor often seen in date syrup made in traditional rural areas (Barreveld, 1993; Belguedj, 2015; and Houssni, 2022).



Figure 1.11. Traditional process for date syrup production : **a)** sorting, **b)** cleaning by water rinse, **c)** putting the date container in, **d)** filling the extraction container, **e)** stirring during cooking, **f)** 1st Rough filtration of the mixture, **g)** 2nd fine filtration of the 1st cooking extract, **h)** Transfer of dates from the 1st to 2nd cooking to the 2nd extraction container, **i)** 2nd cooking of dates, **j)** filtration of residues, **k)** initial torsion pressure of date residues, **l)** semi-mechanical supplementary pressure, **m)** concentration of the date extract by evaporation, **n)** hot bottling, **o)** traditional date syrup (Belguedj, 2015).

Although respectful of tradition, the artisanal methods below are often limited in performance and quality control, which can hurt market competitiveness. Algeria has developed

a mechanized date processing industry to overcome processing limitations. Advanced technologies help factories optimize production, quality, and product shelf life. These methods include mechanical date syrup extraction and controlled thermal treatment. These innovations allow for larger date syrup production with standardized organoleptic and physico-chemical properties for export markets. We have discussed in this section the evolution of the process from a traditional method to an industrial one:

The first factory was established in 1953 and developed in 1969, which is primarily inspired by the reference works of the two pioneers in the field of dates and date palms in Iraq, as mentioned in the three references used (Al-Bakr, 1982), El-Okaidi (1985), and Bekri (non-dated).

The three most fabrication stage are synthesized below:

1.3.2.1. Mechanical extraction

This system was used in the early industrial-scale date syrup production factories in Iraq, a pioneering country in this field. The first development that took place in the date extract production process was the mechanization of extraction, using a container or a double-walled tank, heated by a steam source to reach high cooking temperatures. The double-walled container held a rotating shaft, allowing a motor to spin at different speeds. This process has evolved rapidly and has significantly contributed to the efficiency of extraction.

After that, technological development focused on improving the type of container and the power of the engine, which allowed for even higher speeds to be achieved. The engine has also been refined by transitioning from a simple propeller to more complex ones, with right-curved or right-handed shapes, and then to sharp propellers and turbochargers. These major developments have played a crucial role in optimizing the extraction process.

The objectives of this extraction system is to find a method to increase the extraction of sugars from dates on a commercial scale, and to develop method to increase the surface area of dates by cutting them, in order to enhance the extraction surface, and also to optimize the extraction of sugars from dates and their concentration.

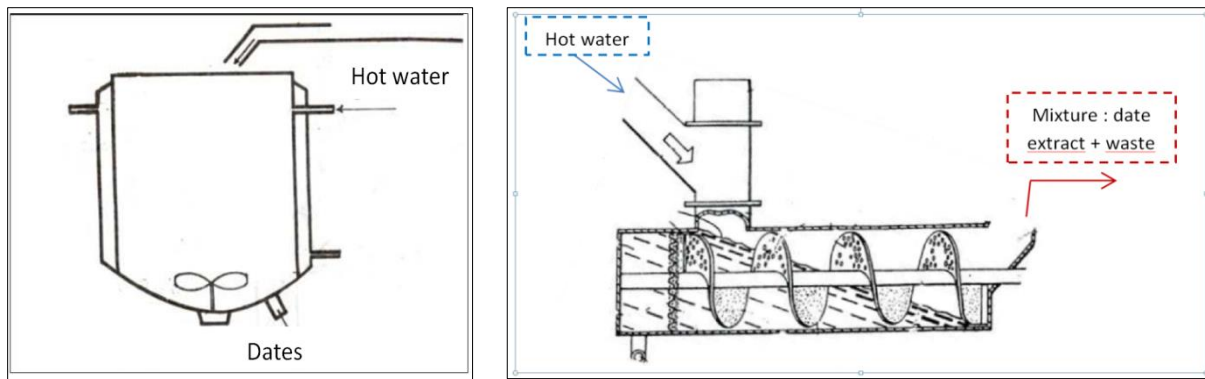


Figure 1.12. Industrial process for date juice extraction

The extraction mechanism for date extract and sugar extraction requires addressing the following questions:

✓ **Amount of water used for extraction**

This refers to the relationship between the amount of water and dates for sugar extraction. This relationship generally ranges between 1:1, 1:2, 1:2.5, or 1:3, depending on whether the extraction is done in one or multiple steps.

✓ **Extraction stages**

The extraction can be done in a single step, in two steps, or in multiple steps to improve the economic yield of the process.

✓ **Time required for extraction**

It is essential to determine the time needed for extraction at one or multiple stages and to assess the economic advantage based on this time.

1.3.2.2. Filtration

After this process, an operation is carried out to remove all materials, residues, and impurities from the juice through a filter press or a drum filter. The two filters serve to eliminate about 85% of the materials, residues, and impurities from the juice. After this operation, the juice is ready to be processed through ion exchangers and activated carbon to remove certain proteins, colorants, and undesirable substances.

1.3.2.3. Concentration of the date juice by evaporation

Evaporators are heat exchangers used to remove excess moisture from certain products such as juices, tomato concentrate, and the production of concentrates. The heating process is conducted using hot substitute water to compensate for the amount of water evaporated. This can be done in a single step or in multiple steps, depending on the needs, using the steam produced by the first evaporator to heat the second. It is important to mention that using

a parallel configuration of evaporators allows for an increase in the capacity to recover condensed water.

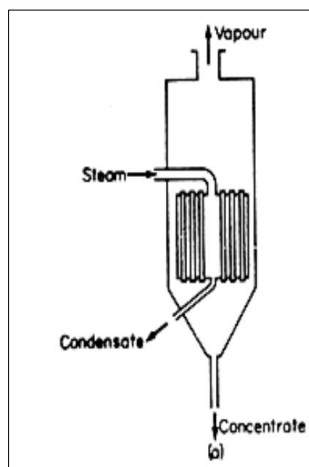


Figure 1.13. Industrial process for date juice concentration by evaporation

The following table presents some date syrup production units in Algeria as well as in other Arab countries.

Table1.1: Some examples of date syrup industrial production company in Algeria and others countries

Region	Region	Processing plant name	references
Algeria	Setif	Eurl Prestige dattes	Anonymous, non-dated
	Hassi Messaoud	El Faiza sarl	Anonymous, non-dated
	Biskra	Ametna sarl	Anonymous, non-dated
		Biodattes Algerie	Anonymous, non-dated
Saudi Arabia	Al-Hassa	Al- Jawharia date factory	Table Saudi Industrial Development Fund (2010)
		Al-hassa company for food industry date processing plant	
	Riyadh	Amal Al-khair dates packing and packaging factory	
	Qassim	Nadheed Dates Factory	
Iraq	Karbala	-	El-Okaidi (2010)
	Baâqouba	-	
	El Fayhaa	-	

1.3.3. Date syrup uses

1.3.3.1. In traditional phytotherapy

In their paper review titled "Dates: nutritional interest", Benchelah and Maka (2008) agree that highly concentrated preparations of date syrup have demonstrated therapeutic properties. This syrup has been found to hold a sedative effect on youngsters. Furthermore, it is used for treatment of neurological disorders and infections which affect broncho-pulmonary diseases. Date syrup is produced year-round. Belguedj (2014) conducted a survey on householders

and found that date syrup is commonly used to treat coughs and support people with anemia. This explains why its production increases during the winter period. Boudjrada and Zidi (2023) conducted a survey on 161 hospitalized patients to investigate the therapeutic uses of plants. Their findings confirmed our results, revealing that 6.3% of the study population utilized plants as a treatment for deficiency anemia. Furthermore, Houssni (2022) reported that the most common uses is as a dietary supplement and energy source for the convalescence of the sick and for women both during pregnancy and after childbirth and to promote breastfeeding. It is also recommended for the protection of the digestive system and the prevention of gallstones.

1.3.3.2. Culinary uses

Benchelah & Maka (2008) reported date syrup use to soften dishes and drinks, also, in the survey carried out by Belguedj (2014), 66.66% of households replacing white sugar by date syrup in cake preparation, partially or entirely, or generally consumed as a substitute for bee honey, being an expensive product (Houssni, 2022), fresh or slightly heated at mild heat, accompanied by traditional bread, or as a flavor agent for milk, juice or pastry. The method of preparation highlights the adaptability of *Rob* and its incorporation into everyday meals, where it acts as a complement to staple meals (Figure 1.12).



Figure 1.14. Traditional breakfast with date syrup (Houssni, 2022)

Chapter 2

Overview of some theoretical concepts on experimental designs and Box-Behnken Design (BBD)

2.1. Response Surface Methodology (RSM)

The so-called one variable or factor at a time (OVAT/OFAT) method, which assesses the influence of an experimental parameter while holding the other variables constant, has traditionally been the basis for optimizing material characteristics and process parameters in the analytical and pharmaceutical chemistry fields. This process is complex, involving multiple excipients and stages (Beg & Akhter, 2021).

We adjust each factor until it reaches its optimal level. The level is fixed. Next, we adjust the other factor until it reaches its optimal value and maintain it there. We repeat the process with another factor: the OFT method necessitates numerous experiments, leading to increased costs in terms of time, reagents, and research materials. After each trial run, this method draws experimental conclusions by comparing the observed outcome to the previous result, making factor effect estimation less precise. If factors interact and their effects depend on each other, this suggests interaction, and this approach may miss the best settings. OFAT cannot estimate factor interactions, which can result in underestimating or misinterpreting the results and mislead process optimal conditions; furthermore, ignoring these factors' relationships can lower product quality (Wahid & Nadir, 2013).

These limitations necessitate the use of multivariate statistical methods to optimize analytical and pharmaceutical processes. The Design of Experiments (DoE) is a commonly used systematic tool. This latter method employs statistical principles and predefined objectives to conduct minimal experiments that yield the most information for product and process development (Beg et al., 2019).

Box and Wilson created the Response Surface Methodology (RSM) of DoE in 1951, to improve the efficiency of industrial processes (Dean et al., 2017). RSM uses polynomial models, which are usually quadratic, to fit experimental data. These lets us model and predict how a system will behave based on many variables (Bezerra et al., 2008). This technique works well when more than one variable (independent variables) has an effect on the interest response(s) (dependent variables) at the same time. It helps to see how the different variables are affecting each other. The fundamental purpose of Response Surface Methodology (RSM) is to improve the response by finding the best experimental circumstances while using the

fewest tests possible (Sano et al., 2020). Also, RSM can make the optimization process better by handling these interactions well. This leads to more reliable results and fewer experiments needed. To improve process efficiency, the chemical and analytical literature often uses linear or quadratic models that combine the linear, quadratic, and interaction impacts of several components (Sudha et al., 2017).

2.1.1 Terminology

Before addressing response surface uses in analytical method optimization, it's important to define some key terms (Berger et al., 2018):

- The specific area of study that requires examination in an experiment is known as the “**experimental domain**”. The lower and upper bounds of the experimental variables under investigation determine the domain.
- A “**matrix**” containing various combinations of the variables' level under study determines an “**experimental design**”, which is a defined set of experiments.
- An experiment can alter “**factors**”, also known as “**independent variables**”, independently from each other, which are controlled in an experiment to observe their effect on the response. Common independent variables include: extraction temperature, microwave irradiation power, extraction time, solvent concentration, solvent/solid ratio, pH, concentration of reagents or substrate, enzymatic activity, operating system pressure, speed stirring, etc.
- The term “**levels of a variable**” refers to specific values at which experiments are required. The variable levels in an extraction process optimization are defined as follows: solvent concentration: 40% (low), 60% (medium), 80% (high), and extraction time: 30 minutes (low), 60 minutes (medium), and 90 minutes (high). These levels structure experiments to assess the impact of each variable on the process.
- “**Responses**”, also known as “**dependent variables**”, are the quantifiable values obtained from experiments. Common indicators include analyte recovery (extracting yield of polyphenols, total antioxidant activity, flavonoid concentration), biomass production, final acidity level, texture of a food product, and total sugar content, among others.
- The “**residual**” refers to the divergence between the predicted and experimental response values under specific and fixed conditions. We should expect low residuals when fitting an efficient mathematical model to experimental data.

- **“Polynomial model”** In the RSM, the relationships between the factors and the responses are often modeled using polynomials, usually of the second order (quadratic). This allows for capturing linear, quadratic, and interaction effects between the factors.
- **“Response Surface”** is a graphical representation of interactions between two factors and a response. It helps to visualize optimal conditions.
- **“Critical Points”** are the values of the factors for which the response reaches a minimum, a maximum, or a seat point, crucial for optimization.
- **“ANOVA (Analysis Of Variance)”** allows verifying the statistical significance of the effects of factors and their interactions in the polynomial model.

2.1.2 Codification of the levels of the variable

As reported by Sen (1997), the analysis of the obtained experimental results is carried out on normalized (coded) variables. Normalization of variables is the transformation of the independent variable real values into dimensionless values according to Equation (2.1); wish defined the relationship between the coded and real values:

$$x_i = \frac{X_i - X_0}{\Delta x} \quad (2.1)$$

Where:

- X_0 : is the real value of the independent variable at the center point;
- Δ : is the step change value;
- x_i and X_i : are, respectively, the least encoded dimension and the real values for its independent variables, at the center points.

The codes are determined based on the specific range of each factor, as indicated in table 2.1.

Table 2.1: The relationship between the encoded and actual values of the variables (Napier-Munn, 2000).

Code	The variable 's actual value
$-\alpha$	X_{min}
-1	$[(X_{max} + X_{min}) / 2] - [(X_{max} - X_{min}) / 2\beta]$
0	$[(X_{max} + X_{min}) / 2]$
$+1$	$[(X_{max} + X_{min}) / 2] + [(X_{max} - X_{min}) / 2\beta]$
$+\alpha$	X_{max}

β is $2^{n/4}$; n is the number of variables (concentration, time and temperature), and $n=3$.

2.1.3 Polynomial model

As reported by Beg & Akhter (2021), the most basic model that can be utilized in Response Surface Methodology (RSM) is founded on a linear function. In order to apply it, it is imperative that the obtained responses are accurately aligned with the following equation (2.2) (Box & Behnken, 1960):

$$Y = \beta_0 + \sum_{i=1}^k \beta_i X_i + \sum_{i=1}^k \beta_{ii} X_{ii}^2 + \sum_{ij}^k \beta_{ij} X_i X_j + \varepsilon \quad (2.2)$$

Where:

- Y : is the response,
- β_0 : is a constant term,
- β_i : are the coefficients of the linear terms (main effect),
- β_{ii} : are the coefficients of the quadratic effects,
- β_{ij} : are the coefficients of the interaction effects, (the variables i and j range from 1 to k),
- X_i : are the levels of the factors,
- ε : is the residual error.

2.2 Steps for the application of the RSM

The application of the RSM follows several steps to ensure accurate results. These steps include a preliminary study, the selection of the experimental plan, the mathematical processing of data, model verification, and the determination of optimal conditions.

2.2.1 Preliminary Study

It enables the choice of factors that have an impact on the response. Prior to determining the ranges of variation of the factors, it may be necessary to conduct a literature review or preliminary experiments (Myers, 1999).

2.2.2 Choice of the experimental design

The choice of the experimental design is crucial in order to ensure an effective modeling of responses based on the studied factors, and to explore the interactions between factors. Among the experimental designs commonly used in response surface methodology (RSM), the central composite design (CCD) and the Box-Behnken design (BBD) are the most suitable for optimization objectives (Jensen, 2017). The choice of the plan therefore directly depends on the specific objectives of the study (Bukowski, 1995):

- ✓ *Central Composite Design (CCD)*: This design incorporates axial and central points to model quadratic relationships. The CCD is particularly advantageous when the goal is to explore a vast response space, as it includes central points, axial points, and points located

on the edges of the experimental cube, allowing for a thorough evaluation of interactions between variables as well as a more precise detection of quadratic effects. CCD will be better suited for a more detailed optimization with a larger number of variables and levels to explore.

- ✓ *Box-Behnken Design (BBD)*: This design does not include extreme points, which decreases the number of experiments that need to be carried out. The Box-Behnken design is often preferred when experimental resources are limited, while allowing for a robust estimation of interactions without including potentially extreme points that may be far from the practical optimization region. If the goal is to achieve fine optimization with a limited number of experiments, the BBD can be recommended.

2.2.3 Mathematical and statistical processing of data

After collecting the data, it is analyzed using a second-order polynomial model, allowing for the exploration of the relationships between the factors and the response. Analysis of variance (ANOVA) is used to assess the statistical significance of the effects of factors. If the model is suitable, it can be used to predict the response under various conditions (Montgomery, 2017).

2.2.4 Verification of the adjusted theoretical model

Model verification involves comparing the values predicted by the model to the experimental values. If the residuals values are randomly distributed, the model is considered reliable. Cross-validation can also be used to assess the efficiency of the model (Khuri & Cornell et al., 2018).

2.2.5 Determination of optimal conditions

Optimization involves identifying the conditions of the factors that maximize or minimize the response (Ardakani & Wulff, 2013).

2.3. Box-Behnken Design (BBD)

Box Behnken Design (BBD) is one of the most commonly used designs in Response Surface Methodology (RSM) due to its efficiency and low experimental cost.

2.3.1. BBD Graphical presentation for second-degree models BBD

Box-Behnken designs (BBD) are a class of rotatable quadratic designs based on three-level incomplete factorial designs. The experimental points are located on a hypersphere equidistant from the central point, as exemplified for a three-factor design optimization with its 13 experimental points in Fig. 2.1, which presents the Box–Behnken design for three-variable (Prakash et al., 2013).

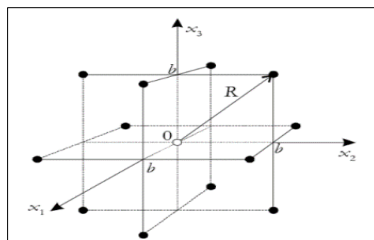


Figure 2.1. Box-Behnken Design ($k=3$)

The experimental points are at the midpoint of the edges of each side of the cube (Figure 2.1). This plan includes 12 essays to which one (or more) central point(s) can be added. The matrix of table 2.2 indicates these twelve trials accompanied by a single central point. In experimentation, we usually achieve 3 or 4 points at the center.

Table 2.2.: A standard design matrix of a Box-Behnken Design for three-factors three-levels (Beg & Akhter 2021)

Run	X_1	X_2	X_3
1	-1	-1	0
2	-1	+1	0
3	+1	-1	0
4	+1	+1	0
5	-1	0	-1
6	-1	0	+1
7	+1	0	-1
8	+1	0	+1
9	0	-1	-1
10	0	-1	+1
11	0	+1	-1
12	0	+1	+1
C	0	0	0
C	0	0	0
C	0	0	0

Note: X_1, X_2, X_3 are three independent factors, -1, 0 and +1 are the levels of each of the three factors

As defined by Mee (2000), a characteristic of Box-Behnken matrices is the fixed number of values that each factor takes: The various levels will subsequently be rated (-1, 0, 1). These matrices are created by adding balanced incomplete blocks to complete factor matrices. Observe that there are center points as well.

Table 2.3: Number of experiences for BBD (Vivier, 2002)

k	3	4	5	6	7
V_{bb}	13	25	41	49	57

The coordinates of the experimental points are tabulated for each of these configurations since the construction of the Box-Behnken matrices is not fixed for any value from k to another.

For each value of k , the table below shows how many more experiments need to be done to reach this point in theory (Zhang et al., 2011). Concerning the number of experiences at the central point, by taking only one point at the center, the number of experiments required to carry out a Box-Behnken design for k factors is given below.

Table 2.4. Number of experiences at the central point (Vivier, 2002)

k	3	4	5	6	7
Number of experiences at the center point	3	3	6	6	6

2.3.2. Box Behnken Design (BBD) in the food industry

Box-Behnken Design (BBD) is a statistical tool that has proven effective in the food industry for optimizing polyphenol extraction conditions, particularly from fruit, by modeling the interactions between several factors, such as solid-to-solvent ratio, temperature, and extraction time. BBD has the potential to considerably improve phenolic compound yields. For example, Koraqi et al. (2023) conducted an investigation on the extraction of total phenolic compounds from strawberries (*Fragaria x ananassa* Duch.) with the aim of optimizing extraction parameters using BBD. Their findings suggest that this approach may result in maximum polyphenol and flavonoid contents, while also minimizing costs and time. Similarly, Jeganathan et al. (2014) employed BBD to enhance the extraction of polyphenols from red grapes, examining the collective impact of temperature, time, and solid-liquid ratio, with the objective of maximizing the yields of anthocyanins, phenolic compounds, and flavonoids. Also, Prgomet et al. (2019) demonstrated the potential of BBD in optimizing the extraction of polyphenols from almond by-products, suggesting ideal conditions for extracting compounds with high antioxidant properties.

Regarding optimizing the aqueous extraction of natural soluble compounds from fruit, this method models the interactions between several factors such as temperature, extraction time and enzyme concentration to maximize the yield and functional properties of extracts. For example, Sonawane et al (2020) used BBD to optimize the enzymatic extraction of bael fruit juice, achieving ideal conditions to maximize juice recovery and nutritional properties. Prakash Maran and Manikandan (2012) also applied BBD for the aqueous extraction of pigments from cactus fruit (*Opuntia ficus-indica*), optimizing betacyanin and betaxanthin pigment contents, with specific temperature and time conditions. Finally, Patel et al (2022) used BBD to model the extraction of Indian jujube juice using cellulase, demonstrating a significant increase in juice yield, polyphenols and antioxidant activity. These studies demonstrate the effectiveness of BBD in optimizing aqueous extraction processes for soluble natural compounds in the food industry.

Experimental
part

This work was carried out in several research structures, mainly at the “Laboratory of Biomathematics, Biophysics, Biochemistry and Scientometrics (BBBS)” of the University of Bejaia, as well as at the “laboratory of date palm technology” of the Centre for Scientific and Technical Research on Arid Regions (CRSTRA) of Biskra, and the “laboratory of the department of instrumental analysis and environmental chemistry” of the Institute of General Organic Chemistry (IQOG-CSIC) of Madrid in Spain.

Chapter 3: Morphometric, physicochemical, and phytochemical characterization of the date palm fruit (*Mech-Degla* c.v), and evaluation of its free radical scavenging activity *in vitro*

It is known that date fruits have a significant amount of energetic and bioactive compounds, namely sugars and polyphenols. The objective of this chapter is to evaluate the morphometric and physicochemical attributes of the chosen date palm fruit variety "*Mech-Degla*". Afterwards, the extraction's optimization of the total phenolic compound amount of the date pulp is conducted using Microwave Assisted extraction «MAE» in conjunction with the response surface methodology (RSM). The extraction yield of the phenolic compounds of the resulting extracts is then compared to those of the extracts produced using Conventional Extraction «CE» and Ultrasound Assisted Extraction «UAE» Finally, In order to ascertain the phyto-composition of the optimized phenolic extract, the high-performance liquid chromatography coupled to mass spectrometry in tandem with Ionization by electro-spray (UPLC-ESI-MS/MS) technique was employed. Ultimately, the antioxidant activity *in vitro* was evaluated.

3.1. Material and methods

3.1.1. Chemicals

The following items were purchased from Sigma-Aldrich (St. Louis, MO, USA): phenolphthalein, ethanol, Glucose, Fructose, methanol, phenyl beta glucoside, hydroxylamine chloride in pyridine, 2,2-diphenyl-1-picrylhydrazyl radical (DPPH), Folin–Ciocalteu reagent, gallic acid, sodium carbonate, sodium hydroxide, hexamethyldisilazane (HMDS), trifluoroacetic acid (TFA), acetone, and heptane. While, Sulfuric acid 96 (%), phenol, 3,5-dinitrosalicylic acid, gallic acid, were acquired from merck illipore.

All the utilized chemicals and reagents were of analytical grade. Glucose, fructose, and sucrose, for chromatographic for GCMS quality.

3.1.2. Plant material

In this investigation, we used the "*Mech Degla*" date palm variety from palm groves of *Oued-Righ* valley in southeastern Algeria, collected at the final ripening stage. This choice is explained by the relative abundance of this variety on the Algerian territory, as well as its low value on the local market, also, its dry consistency witch improve its ability for long-term preservation also, its powdery texture enhance the date pulp ability for powder preparation, as well as its nutritional and gustative quality. The dates were rinsed using distilled water, pitted manually, crushed and dried in an oven at 40°C for about 48 hours until obtaining a constant weight, then grounded use an electric grinder to achieve a powder that is extremely fine, then sieved. Diagram of fabrication and photography of illustration were shown in figure 3.1 and 3.2, respectively. Finally, the date pulp powder was held at -18 °C until it is needed.

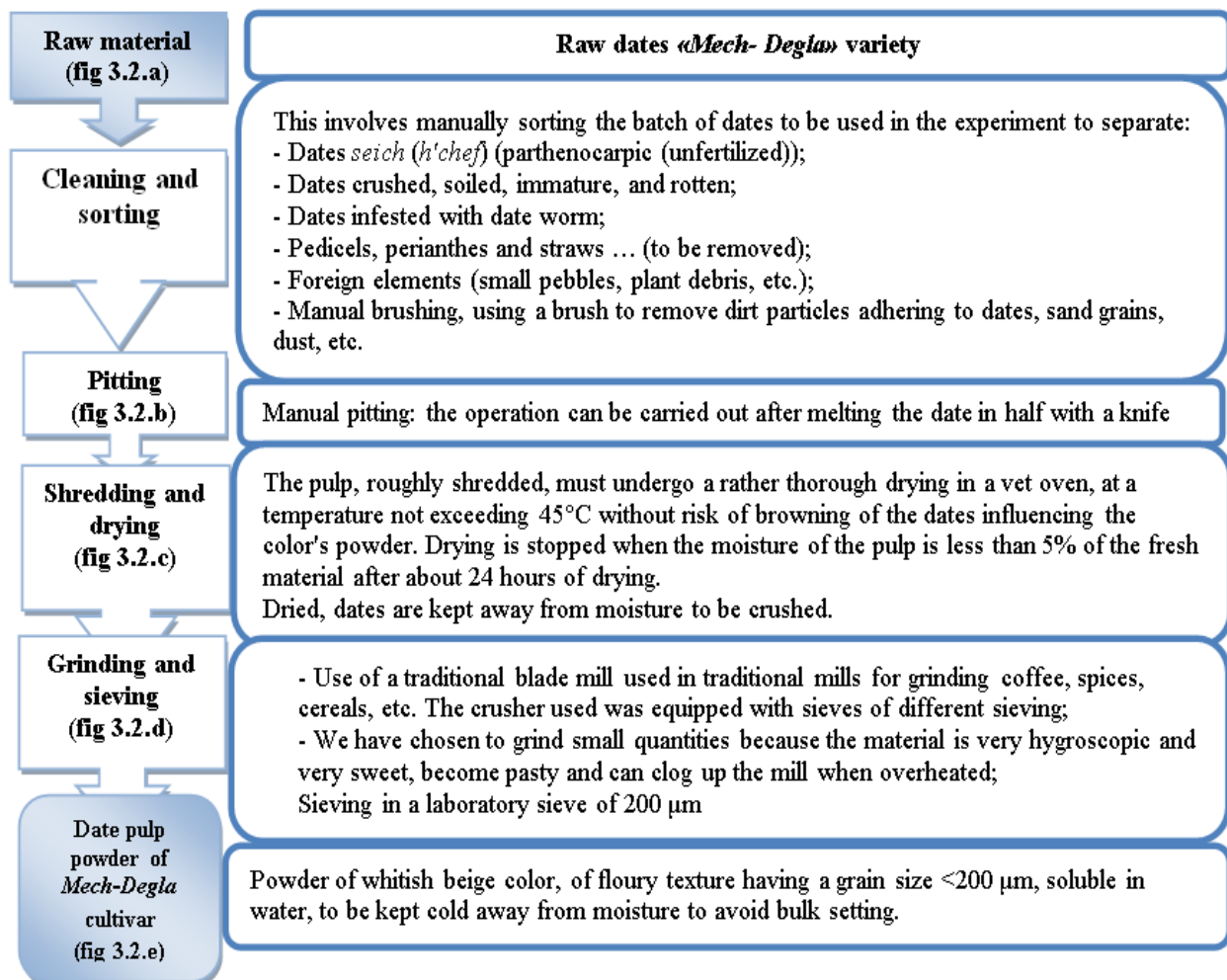


Figure 3.1: Flow chart for preparation of date pulp powder from “Mech-Degla” variety

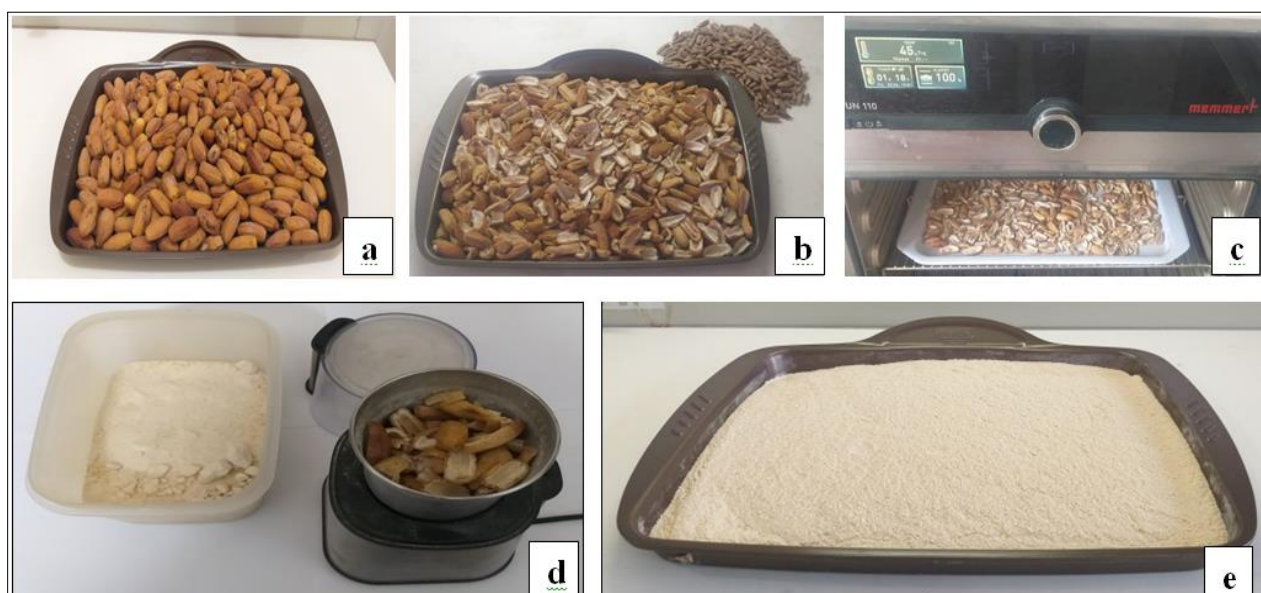


Figure 3.2: Photography of the date pulp powder processing stages from “Mech-Degla” date fruit variety

a) Raw material, b) Pitting, c) Shredding and drying, d) Grinding and sieving, e) Date pulp powder of

'Mech-Degla' variety

3.1.3. Morphometric characterization

The date fruits were morphologically characterized using the methodology outlined by Belguedj (2002) and Muralidhara et al. (2016), and succinctly cited as follows: shape, color (at *tamar* stage, valued visually), consistency and texture, average weight (using precision laboratory balance) and sizes (using digital calipers, mark KENDO, 150 mm and 6", with precision of 0.05 mm) of the entire fruit and seed.

3.1.4. Physico-chemical analyses

3.1.4.1. Moisture content (NF V 03-601)

Moisture content was determined following the desiccation method: 5 g of the date pulp is desiccated in a porcelain capsule at 105°C for about 24 hours in an oven with ventilation until the weight remains steady. The results are expressed as % of moisture compared to fresh matter, as represented in equation 3.1:

$$\text{Moisture (\% FW)} = (m_1 - m_0) * 100 / P \quad (3.1)$$

Where:

m_1 : Capsule weight + fresh mass of the date pulp previous to drying (g);

m_0 : Capsule weight + fresh mass of the date pulp subsequent to drying (g);

P: weight of test sample (g).

3.1.4.2. pH (NF V05-108, 1970) and titratable acidity (NF V05-101, 1974)

In a beaker, 10 grams date pulp was combined with 75 ml distilled water. Electrodes were submerged deeply in pH 4, 7, and 9 buffer solutions after calibrating the pH meter. pH meter measures the potential difference between two submerged electrodes to determine pH.

For titratable acidity, 50 ml of distilled water is added to $m = 25$ g of date pulp, heated to 60°C for 30 minutes, transferred to 250 ml volumetric flask, dilute, filter twice, and acido-basic titration of a determined volume V_0 of the filtered aqueous extract with NaOH 0.1N solution and 5 drops of phenolphthalein until permanently pink (20 sec). This formula determines titratable acidity in equation 3.3:

$$\text{Titratable acidity (gram of citric acid/ 100g of date pulp)} = (250/m) * (V_1/10) * (100/V_0) * 0.07$$

Where:

M: mass of pulp taken (g);

V_1 : volume of 0.1N NaOH sodium hydroxide solution used (ml).

V_0 : volume of test sample (ml).

3.1.4.3. Total sugar content and reducing sugar content

The method outlined by Dubois et al. (1956) was employed to ascertain the total sucrose content. 1 ml of the extract (diluted in distilled water) was placed in the test tube,

0.5 ml of phenol (5%) then 3 ml of concentrated sulfuric acid was added and the solution was mixed. After incubation at 40°C for 30 min, the absorbance was measured at 490 nm against a blank (made as reported for the sample but with 1ml of distilled water), by using an UV-Vis Spectrophotometer (Model Cintra–GBC 10, Australia) as Glucose was used as a standard for the calibration curve to express the total sugar content as mg of glucose/100g of date pulp (Figure 1 in annex 1).

The method outlined by Miller (1959) was employed to ascertain the reduction in sugar content; the test tube was filled with 1 ml of the sugar extract, 1 ml of DNS solution and mixed. After incubation at 100°C for 10 min, 10 ml of distilled water is added to stop reaction, the absorbance was measured at 540 nm against a blank (made as reported for the sample but with 1ml of distilled water), by using an UV-Vis Spectrophotometer (Model Cintra–GBC 10, Australia) as Fructose was used as a standard for the calibration curve to express the total sugar content as mg of Fructose /100g of date pulp (Figure 2 in annex 1).

3.1.4.4. Glucose, fructose, and sucrose

For GC-MS analysis, the preparation of the date sample for injection is performed according to the protocol described by Abdul-Hamid (2019): a mixture of 2 g of date powder and 20 mL of absolute ethanol was sonicated in an ultrasonic bath with a stainless steel tank (type 1.4301), and internal dimensions (300 mm length, 240 mm wide and 65 mm deep, giving a nominal capacity of 4.3 liters. The unit operates at a fixed frequency of 35 kHz, with a peak power of 560 W and a power supply of 230 V \pm 10%, 50/60 Hz. The sample is treated for 1 h at a controlled temperature (below 40 °C). Then, the mixture was macerated with magnetic stirring at room temperature for 24 h. The extract was then filtered using Whatman filter paper N° 4 in a Buchner funnel, then centrifuged at 4500 tr/min for 15 min.

Following a methodology inspired by the work of Ruiz-Matute et al. (2010): a 1 μ L aliquot of diluted date-pulp extract was subjected to GC-MS analysis to quantify the major sugars: sucrose, glucose and fructose. Prior to injection, samples were derivatized in two stages: first by reaction with 350 μ L of hydroxylamine chloride solution (2.5% in pyridine) for 30 minutes at 75°C, then by successive addition of 350 μ L hexamethyldisilazane and 35 μ L trifluoroacetic acid, incubated at 45°C for 30 minutes. These transformations converted the carbohydrates into their oximic trimethylsilyl derivatives (OTMS).

Analysis was carried out on a GC-MS system consisting of an HP 6890 gas chromatograph combined with an HP 5973 quadrupole mass detector (Agilent Technologies, Palo Alto, CA, USA), using helium as carrier gas at a constant flow rate of 1 mL/min. Compounds were separated using an SPB-1 capillary column (fused silica, cross-linked methylsilicone stationary phase)

supplied by Supelco (Bellefonte, PA, USA), with dimensions of 25 m × 0.25 mm and a film thickness of 0.25 μm. The oven temperature program was adapted with minor adjustments to that reported by Ruiz-Matute et al. (2010): an initial isothermal phase at 200°C for 5 minutes, followed by a gradient of 15°C/min up to 270°C, then an increase to 290°C at a rate of 1°C/min, and finally a rise to 310°C maintained for 15 minutes. The injector, heated to 300°C, operated in split mode at a ratio of 1:60. Detection was carried out in electron ionization mode (70 eV) with a scan range of m/z 50-650. The mass spectrometer transfer line was stabilized at 280°C. For quantification, calibration curves were established using standard solutions of sugars in the estimated concentration range in date extracts, with phenyl-β-D-glucoside employed as the internal standard for calculating response factors (RF). Each sample was injected in duplicate, and compound identification was based on comparison of retention times and mass spectra of OTMS derivatives with those of reference standards.

3.1.5. Phytochemical analyses

3.1.5.1. Extraction of date polyphenols

The objective of this section was to optimize the extraction of phenolic compounds (TPC yield) from date pulp powder applying Microwave-Assisted Extraction «MAE» employing a Box-Behnken Design “BBD” of Response Surface Methodology. Laguerre (2020) and Chen et al. (2024) highlighted the advantages of MAE, which converts electromagnetic energy into heat energy inside the fruit. This allows rapid and constant heating by absorbing and converting energy into heat throughout the fruit, unlike conventional methods that use conduction and convection from the surface. This method reduces processing time and preserves plant material's nutritional and sensory qualities by minimizing overheating and carbonization. We compared the findings to CE and UAE.

3.1.5.1.1. Conventional Extraction «CE»

The phenolic components of the date pulp powder were extracted using the methodology outlined by Arroy et al. (2017) with minor alterations. A mixture of 1 g of date pulp powder with 50 milliliters of methanol (80%) (v/v), and the extraction procedure was stored in obscurity at ambient temperature (~25°C) with magnetic stirring (figure 3.3) for 60 min.



Figure 3.3: Extraction of date pulp polyphenols using Conventional Extraction «CE» method

3.1.5.1.2. Ultrasound Assisted Extraction «UAE»

As shown in figure 3.4, date pulp phenolic components were extracted using a Vibracell (VCX 750,115 PB, SONICS, Newtown, Connecticut, USA) ultrasonic device (maximum net power output: 750 W, 20 kHz, maximum amplitude: 75%, 180 μm) with slight modifications, following Dahmoune et al. (2014). A microtip (6 mm) was immersed in one gram of date powder and 50 milliliters of methanol at 80% (v/v) and subjected to ultrasonic waves at 60% at room temperature for 60 min under an alternative rhythm (10 sec power on, 5 sec power off to prevent super-boiling and thermal degradation). The tip-vessel bottom distance was 1 cm.

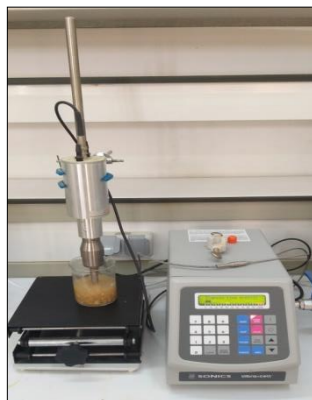


Figure 3.4: Extraction of date pulp polyphenols using Ultrasound Assisted Extraction «UAE» method

3.1.5.1.3. Microwave Assisted Extraction «MAE»

To carry out the experiment, a water condenser was positioned on top of a multimode domestic microwave (MAXMOS23S, Maxipower, China) operating at 2450 MHz, with a maximum delivered power of 900 W, and cavity dimensions of 28.1 cm height, 48.3 cm length, and 38.7 cm depth in our laboratory (figure 3.5). One gram of date pulp powder was added to different type of solvent (acetone, methanol, ethanol, and water) and different concentrations (20, 40, 60, 80 and 100 %). The samples were subjected to irradiation under

different conditions of Solid to liquid ratio as (1:30, 1:40, 1:50, 1:60 and 1:70 g/ml) microwave power (180, 360, 540, 630 and 720 Watts), and treatment time (3, 4, 5, 6 and 7 min), under an alternative rhythm (10 Sec power on, 5 Sec power off to prevent super-boiling inducing thermal deterioration of the matrix and also the loss of solvent in the course of microwave irradiation).



Figure 3.5: Extraction of date pulp polyphenols using Microwave Assisted extraction «MAE» method

Following each essay, the extract was subjected to filtration utilizing Whatman filter paper (no. 4), and the solution' volume was then adjusted to 50 ml with methanol 80% and kept at 4°C. Within the context of the complete phenolic extraction, the solvent type and concentration of the solvent, the solid/liquid ratio, the microwave irradiation power, and the irradiation time on the total phenolic amount was investigated. The parameters exerting the most significant influence on polyphenol extraction were identified for the response surface methodology analysis.

3.1.5.2. Box-Behnken design

Applying MAE, in order to evaluate the impact of three independent variables (X_1 : Methanol concentration (%), X_2 : Microwave power (Watt) and X_3 : irradiation time (min)) on the extraction recovery of total phenolic compounds (TPC) from date pulp samples, a BBD of RSM was set up using the software of Minitab (version 17.1.0) . This plan allows a complete analysis of the total number of experiments and any interaction between variables. The experimental design consisted of three level-three factors (coded -1, 0, and 1) and three replicates at the central point, for a total of 15 data points. This configuration allowed studying the linear and quadratic effect of each variable, as well as the interactions between them, on the measured response (TPC extraction recovery).

The BBD response (Y) was determined by the extraction yield of phenolic compounds amount (expressed as mg GAE/g DW). Its matrix was carried out using three independent variables at three levels, comprising 15 trials (12 factorial and 3 central) points, as shown in table 3.3. The equation 3.4 delineates the statistical relationship between the encoded and actual values:

$$x_i = \frac{X_i - X_0}{\Delta x} \quad (3.4)$$

Where: X_0 is the real value of the independent variable at the center point, Δx is the step change value, and x_i and X_i are, respectively, the least encoded dimension and the real values for its independent variables (Wakejo et al., 2022). At the center points, three replicates were also measured. Equation 3.5 was used to fit experimental results for a second-order polynomial model:

$$Y = \beta_0 + \sum_{i=1}^k \beta_i X_i + \sum_{i=1}^k \beta_{ii} X_{ii}^2 + \sum_{ij}^k \beta_{ij} X_i X_j + \varepsilon, \quad \text{with } k = 3 \quad (3.5)$$

Where Y is the measured response variable, which in our case is the extraction yield of phenolic compounds amount (expressed as mg GAE/g DW), β_0 is a constant, β_i is the linear coefficient (main effect), β_{ii} is the quadratic coefficient, β_{ij} is the two coefficients of factor interaction, X_i , X_j are the independent variables, and ε is the error.

This experimental design allows evaluating the extraction method' efficiency according to the extraction yield, and determining the optimum operating condition. The experimental data analysis consisted of adjusting a second degree polynomial model to describe the measured response. This model was used to evaluate the effect of variables and their interactions on TPC extraction yield. Through rigorous statistical analysis, the optimal extraction conditions were determined to maximize this yield.

3.1.5.3. Estimation of the phenolic content by the Folin–Ciocalteu test

The measurement of total phenolic compounds amount was performed utilizing the method described by Agourram et al. (2013), with slight modifications: 500 μ l of the phenolic extract or gallic acid standard solutions were combined with 2.5 ml of 1:10 diluted Folin-Ciocalteu phenol reagent After 3 minutes, 2 ml of 7.5% (w/v) aqueous sodium carbonate was added, the mixture was agitated once more, and subsequently allowed to stand at 45°C in the dark for 15 minutes. The absorbance was measured at 765 nm using a UV-Vis Spectrophotometer (Model Cintra-GBC 10, Australia), referencing the appropriate reagent blank.

The total phenol content was estimated from the calibration curve, using gallic acid as the standard (0 to 0.07 mg/ml) (Figure 3 in annex 1), and the findings were represented as milligrams of gallic acid equivalent per gram of dry weight "mg GAE/ g of DW".

3.1.5.4. Verification of the solution and the predicted model

The experiments were conducted under optimal conditions to validate the quadratic equation's ability of forecasting the most accurate response value. Each extraction trial was conducted in triplicate.

3.1.5.5. UPLC-ESI-MS/MS analysis of the phenolic extract

Our optimized PRE were micro-filtered through 0.45 μm PTFE syringe filters and stored at -18°C until the analyses. The chromatographic analysis was performed using a UPLC-ESI-MS/MS Shimadzu 8040 system, known for its very high sensitivity thanks to UFMS technology, coupled with a Nexera XR LC-20AD binary pump. The chromatographic separation was carried out on a Restek Ultra C18 column (150 x 4.6 mm, granulometry 3 μm). The mobile phase consisted of a solvent A consisting of water acidified to a solvent A 0.1% formic acid, and a solvent B of pure methanol. The chosen elution gradient was carried out as follow: from 0 to 0.2 minutes, phase A is maintained at 98%; from 0.2 to 2.5 minutes, the proportion of phase A gradually decreases to 25%; from 2.5 to 4 minutes, the phase A is reduced to 0% and kept constant for 4 to 7 minutes; then, from 7 to 7.1 minutes, the phase A quickly rises to 98% to ensure re-balancing, which is extended from 7.1 to 12 minutes at this same percentage. The mobile phase flow rate was maintained at 0.2 mL/min with an injection volume set at 5 μL .

The conditions of ionization by electrospray (ESI) in electrostatic spraying mode were strictly controlled: CID gas at a pressure of 230 kPa, conversion dynode set to -6.00 kV, transfer line temperature (DL) 250°C , nebulization gas flow rate 3.00 L/min, heat block temperature 400°C , and drying gas flow rate 10 L/min.

The identification of phenolic compounds was carried out based on their characteristic retention times and mass spectra obtained by MS/MS tandem detection.

3.1.5.6. DPPH radical scavenging activity

A modified version of the procedure outlined by Braca et al. (2002) was employed to evaluate the radical-scavenging activities of the date pulp sample, prepared at various concentrations of lyophilized RPE in methanol (50-1600 µg/ml), utilizing DPPH free radical scavenging assay. After thirty minutes, the absorbance was assessed at 517 nm and computed using the equation provided below:

$$\text{DPPH scavenging effect (\%)} = \left[\frac{(A_0 - A_t)}{A_0} \right] \times 100 \quad (3.6)$$

Where:

A₀: absorbance of the negative control (methanol) after 30 min;

A_t: absorbance of the sample after 30 min.

A linear regression analysis was performed to calculate the IC₅₀, or sample concentration (in µg/ml) necessary to lower the initial DPPH concentration by 50%. This is a measure of the samples' capacity to scavenge free radicals on DPPH.

Linear regression (LR) was conducted to determine the IC₅₀, or the methanolic extract concentration (in µg/ml) required to reduce the initial DPPH concentration by 50%. This quantifies the samples' ability to scavenge the free radicals in DPPH.

3.1.6. Statistical analysis

Minitab software (Inc. version 17.1.0) was employed for the statistical evaluation of the influence that each individual factor on the total phenolic content in the single factor experiment utilizing MAE was conducted utilizing analysis of variance (ANOVA), which was then followed by the test of multiple comparison conducted by Tukey's HSD (honestly significant difference). A level of confidence of 95% was maintained, and a P-value of less than 0.05 was utilized in order to ascertain the level of statistical significance. For the purpose of determining whether or not the three mathematical models were accurate and valid, the coefficient of determination R² (%), the adjusted coefficient of determination R² adj. (%), and the lack-of-fit tests were utilized.

3.2. Results and discussion

3.2.1. Morphometric characterization

The physical specifications of the studied date fruit variety including the pomological characteristics were represented in Table 3.1.

Table 3.1. Morphometric characterization of "*Mech-Degla*" dates.

Date fruit (D)	
Weight (g)	6.04 ± 0.05
Length (mm)	31.68 ± 1.06
Inner diameter (mm)	15.54 ± 0.45
Outer diameter (mm)	19.40 ± 0.89
Date pulp (P)	
Weight (g)	5.01 ± 0.27
Date seed (S)	
Weight (g)	1.08 ± 0.10
Length (mm)	23.85 ± 1.75
Diameter (mm)	8.76 ± 0.20
Weight ratios	
Pulp/Date (%)	82.98±3.94
Seed/Date (%)	17.88±1.61

Data are presented as Mean ± SD of ten replications (n=10).

**Figure 3.6:** Photography "*Mech-Degla* variety" of date palm fruit

Figure 3.6 represent the photography of "*Mech-Degla*" date fruit, as described by Belguedj (2002), this variety has a sub-cylindrical shape, slightly elongated and flattened at the base, when ripe, it is rather light beige tinged with a slightly pronounced brown, and it is characterized by a dry consistency and a powdered texture. It should be noted that for large-scale date production, it is crucial to consider the weight of the date; choosing date variety with a high fruit weight is crucial for maximizing the yield of date juice. The average weight of the date studied is near to that reported by Belguedj (2002) (6.5 g) and is composed mainly of pulp (5.01 ± 0.27 g), which represents 82.98±3.94 % of the total weight. Those values are slightly greater than those of Noui (2017), for the date weight (5.12 ± 0.65 g) and the pulp (4.15 ± 0.56 g) with pulp/date ratio expressed as a percentage weight of 80.9 ± 0.02 %.

When comparing other studies, we found that these results were similar to those obtained by Amellal-Chibane et al. (2008) for the weight of the date (6.16 ± 0.89 g), the pulp (5.10 ± 0.81 g) with pulp/date ratio of 82.77 %, and the weight of the seed (1.06 ± 0.10 g) with

seed/date ratio of 17.21 %, the length of the date (35.9 ± 1.97 mm), the diameter of the date (19 ± 2.58 mm), and the length of the seed (24.9 ± 1.2 mm), the diameter of the seed (8.1 ± 0.18 mm), but they were slightly greater than those reported by Noui (2017) for the average weight of the seed (0.97 ± 0.16 g), and the diameter of the date (17.44 ± 0.86 mm), and slightly lower for the length of the date (33.82 ± 2.15 mm). Alternatively, the date length and diameter of our sample were much lower than those reported by Djouab (2017) (36.26 ± 2.35 mm and 18.38 ± 2.86 mm respectively). Environmental variables and agricultural practices, may account for either little or substantial variations (Elhoumaizi et al., 2023). The morphometric data presented may be used to inform agricultural methods and breeding programs, with the aim of enhancing the quality and productivity of cultivated dates.

3.2.2 Physicochemical characteristics

The physicochemical and the biochemical features of the studied date fruit variety were represented in tables 3.2

Table 3.2. Physicochemical attributes of the date pulp "*Mech-Degla*" dates

Characteristics	Value
Moisture content (% FW)	12.64±1.50
Total ash (% FW)	2.05±1.24
pH	5.67±0.19
Titrateable acidity*	0.80±0.02
Total sugar (% FW)	75.03±2.54
Reducing sugar (% FW)	18.43±0.19
Glucose (% FW)	8.1±0.33
Fructose (% FW)	8.8±0.39
Sucrose (% FW)	55.65±3.08

Data shown as mean \pm SD of three replications (n=3); *Results are expressed in g eq. citric ac. /100 g of the date pulp

3.2.2.1. Moisture content

The moisture content of fresh dates is influenced by the frequency and amount of irrigations during the *khalal* stage, the humidity of the air during harvest, and the storage site after harvest. The moisture content of food is a determining factor in selecting the appropriate preservation technique to prevent spoiling.

The proportion of water contained in fruit is an essential parameter to assess their quality. According to the observations of Agboola and Adejumo (2013), low humidity content in dry dates can reduce their attractiveness for some consumers, while high water content promotes faster fruit degradation. Moreover, the classification of dates is largely based on their water content: those with a moisture content below 10% are considered dry, while those

with a content above 20% are classified as soft, according to the criteria put forward by El Sohaimy and Hafez (2010).

Ensuring the quality and stability of the date powder produced is dependent on the appropriateness of date fruits that have a dry pulp consistency and moisture content below 10% throughout the drying process.

Our date sample has moisture content of 12.64 ± 1.50 , this result is close to that given by Belguedj (2002), Amellal-Chibane (2008) and who estimate this content at 13 % and 14.77 ± 1.29 respectively. The variations may be attributed to the water content's instability and, therefore, its structure.

3.2.2.2. pH and titratable acidity

pH is a critical factor in the preservation of food, as it inhibits the proliferation of microorganisms. The development of yeasts and moulds is notably facilitated by a pH level between 3 and 6. The pH of our date pulp is 5.67 ± 0.19 , which is mildly acidic. We obtained a pH of 5.67 ± 0.19 and an acidity of 0.80 ± 0.02 g eq. citric ac. /100 g of the date pulp. These values are compatible with those of Amellal-Chibane (2008) as 5.72 for pH and 0.24 ± 0.05 g eq. citric ac. /100 g of the date pulp. Furthermore, Bousdira's (2007) research on approximately twenty date types indicates that pH values range from 5.2 to 6.2, with a mean of 5.8.

3.2.2.3. Total and reducing sugars

Dates are primarily a carbohydrate food, with a total sugar content of 75.03 ± 2.54 % FW for *Mech Degla* variety. Acourene and Tama (1997) confirm this finding, with total sugar content of 75.10 % FW for *Mech Degla*. Our results are also comparable to those of Belguedj (2002), Amellal-Chibane (2008) and Benamara et al. (2009), who estimated it at 80.01, 77.3 ± 0.36 , and 80 % FW, respectively. Furthermore, Belguedj et al. (2023) reported total sugar contents ranging from 38.5% to 78.5 2.5% FW for seven varieties of dry and soft Algerian dates.

Munier (1973) states that total sugar amount and moisture are the major constituents of dates, and their proportion determines the consistency of the pulp. He suggested a “r” index, calculated from the quotient of total sugar and moisture, to categorize dates into three groups: Soft dates when r is less than 2, semi-soft dates for values of r between 2 and 3.5, and dry dates when r exceeds 3.5.

Consequently, the *Mech-Degla* variety is classified as a dry date, with an “r” index value of 5.93.

In the other hand, the reducing sugar amount is 18.43 ± 0.19 % FW. Belguedj (2002) provides an average reducing sugar amount in dates of approximately 20 % FW; however Noui (2007)

finds a value of 14.29 ± 0.39 % FW. The results position the *Mech-Degla* variety within an intermediate range relative to existing literature references.

Dry dates are referred to as sucrose dates; there exists a statistically significant correlation between the sugar content and the moisture level of the dates. According to Bousdira (2007), the dry variety of dates undergo desiccation on the date palm prior to the enzymatic action of "invertase" on sucrose during the *bser* stage (sucrose conversion stage). The conversion of the latter into inverted sugars (reducing sugars) during the maturation period is partially inhibited due to the low water content in the tissues of the fruit.

According to Amellal-Chibane (2008), a date is considered to be of acceptable physical quality when the weight of the whole fruit is greater than or equal to 6 g, and that of the pulp reaches or exceeds 5 g. In the case of the *Mech-Degla* variety, the average weight of the fruit is 6.04 ± 0.05 g, while that of the pulp is 5.01 ± 0.27 g. Thus, with regard to these criteria, *Mech-Degla* dates meet the accepted physical quality requirements.

3.2.2.4. Glucose, fructose, and sucrose

Analysis of the sugars contained in "*Mech Degla*" pulp using GC-MS quantified the three main carbohydrates: sucrose, glucose and fructose (Figure 3.7 and table 3.2). The results obtained, expressed on a wet basis, indicate an average content of $55.65 \pm 3.08\%$ for sucrose, $8.1 \pm 0.33\%$ for glucose and $8.8 \pm 0.39\%$ for fructose.

Comparison of these results with those of the literature shows an interesting convergence with the data of Messadi (2023 a), who reported a sucrose content of $47.02 \pm 0.58\%$ on a wet basis. Similarly, Kacem-Chaouche (2013), having used HPLC, obtained values of 50.07% for sucrose, 13.44% for glucose and 14.93% for fructose. Although the sucrose content of our sample is slightly higher, the differences remain within a reasonable range and may reflect natural variations linked to geographical origin, ripening stage or post-harvest conditions (Baliga et al., 2011). However, monosaccharide (glucose and fructose) levels in our sample are lower than those measured by Kacem-Chaouche. This discrepancy could be explained by the difference in sensitivity and specificity of the analytical methods use, as affirmed by Alghamdi et al. (2020).

On the other hand, and in the light of what the research team Zhang et al. (2015) explained in their article on the relationship between the level of invertase activity and the amount of individual sugars in date pulp, the high sucrose content in our sample may indicate reduced enzymatic activity (particularly of invertase), limiting the hydrolysis of sucrose into glucose and fructose. It may also reflect a particular physiological state of the fruit, such as a stage of ripening where enzymatic transformation of disaccharides has not yet begun.

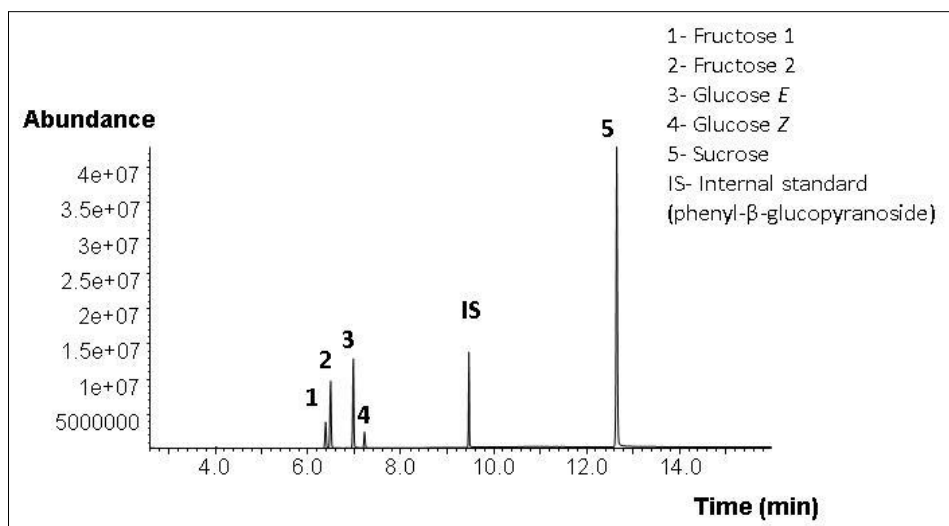


Figure 3.7: GC-MS chromatograms of the sugar profil of *Mech Degla* date pulp

3.2.3. Total phenolic content

3.2.3.1. Effect of independent variables

Phenolic compounds extraction using MAE is significantly affected by processing operating, As shown in the Individual Value Plot of TPC (mg/g DW) vs Extraction parameters in below, the presented results correspond to the mean with the standard deviation calculated from three replicates ($n=3$). The alphabetical annotations (a, b, c) following the averages denote significant statistical distinctions established by the Tukey test. Thus, values with different letters on the same line have significant differences with a probability threshold of less than 0.05 ($P < 0.05$).

- **Effect of solvent type**

The choice of suitable solvents is essential in ecological extraction to maximize the extraction of target compounds. Organic solvents with different polarities, safe for the food and pharmaceutical industries are preferred in order to combine efficiency and safety. Ethanol, methanol, acetone, and their aqueous mixture are commonly used as solvents for extracting polyphenols from plants (Fu et al., 2016). However, the most suitable solvent for extracting polyphenol components from the target plant (in our study, the date pulp powder of the "*Mech Degla*" variety) has not yet been determined due to the varying polarity and chemical properties of the compounds present. Therefore, the four solvents mentioned above are utilized.

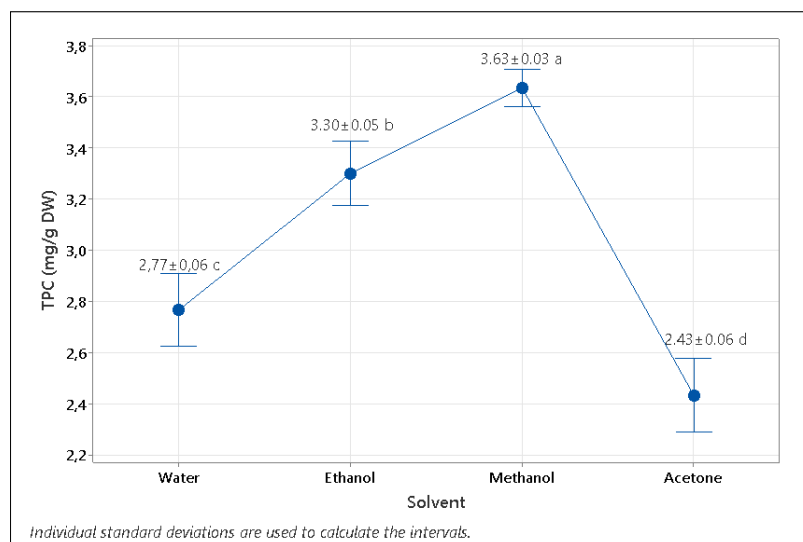


Figure 3.8 : Effect of solvent type on TPC amount

A statistically significant difference was observed among all the solvents used (P-value <0.05); methanol yielded the highest extraction of total phenolic compounds (TPC) with an average yield of 3.63 ± 0.03 mg GAE/g DW (figure 3.8). Based on the obtained results, methanol was the most effective extraction solvent in terms of TPC yield ($p < 0.05$), consequently, it was chosen for the following essays.

The difference in the extracted concentrations can be attributed to the different affinity rates of solvents for the distinct phenolic compounds identified in the fruit, which is due to their chemical properties, polarity and solubility, as well as their amount in the plant matrix (Osorio-Tobón et al., 2020 and Alara et al., 2021). Water, methanol, and ethanol are high protic polar solvents that can dissolve high polar phenolic compounds, inter alia: undecafluorohexanoic acid (acids) for water, catechin and 2-methylamino-phenol (phenols), cholic acid and β -estradiol 17-acetate for (steroids) for methanol, while acetone is an aprotic polar solvent that can be used to extract less polar phenolic compounds such as hydroquinone (phenols) Huffman et al. (2012). As this occurs, more Accurate methods for analysis, such as LC-MS/MS are required to detect and quantify the various phenolic chemicals found in *Mech Degla* date pulp. Acetone can be used in combination with other solvents to extract a broader spectrum of phenolic chemicals.

- **Effect of methanol's concentration**

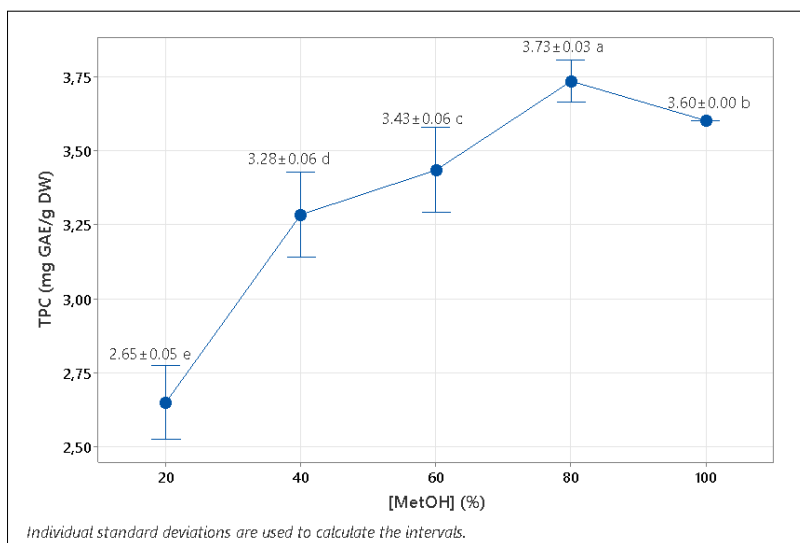


Figure 3.9 : Effect of methanol concentration on TPC amount

As shown in Figure 3.9, an elevation in methanol concentration appears to enhance the extraction; penetration of the extract molecules into the solvent by reducing the dielectric constant of the solution and lowering the energy needed for separation of the solvent molecules (Cacace & Mazza, 2002). In addition, in our case, water enhances slightly the extraction efficacy; the polarity of the methanol/water combination, therefore, improving the extraction of polar polyphenols molecules (Fu et al., 2016). In microwave assisted extraction, the selectivity of extraction can be affected by the polarity of phenolic compounds due to the different dielectric properties of numerous aqueous mixtures of MeOH (Singh et al., 2014). Mixtures with particular coefficients can be used to target specific groups of phenolic compounds; in our study using methanol, in comparison to single solvents, the extraction efficacy of binary solvents (water and organic solvent combined) was slightly greater. The highest extraction yield of TPC (3.73 ± 0.03 mg GAE/g DW) was obtained when using a methanol concentration of 80%, followed by 3.60 mg GAE/g DW at 100 % of methanol (in figure 3.8). Studies have demonstrated that adding a tiny amount of water to a polar solvent helps water penetrate the material's cells, improving extraction heating. This more efficient heating speeds chemical compound migration toward the solvent, boosting extraction speed (Churyumov, 2021). The microwave process is based on the application of electromagnetic fields which induce both conventional thermal transfer phenomena and specific non-thermal interactions within the treated materials. Therefore, 80% was selected for future studies, although the BBD plan included a range of methanol concentrations from 60% to 100%. The work by Marcus (2018) verified that much greater extraction yields for bioactive components

of seaweed and other vegetal materials are obtained when binary solvents, including methanol and water combinations, are used. Because the solvents used in this process complement one another, target chemicals are more easily soluble and transferred in bulk.

- **Effect of solid-to-solvent ratio**

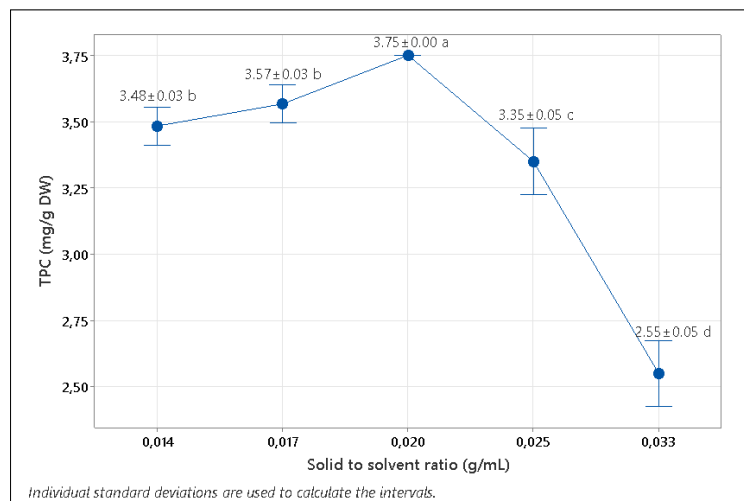


Figure 3.10 : Effect of solid-to-solvent ratio on TPC amount

Beyond the nature and concentration of the solvent, which are decisive elements in the MAE technique, the ratio between solid matter and solvent volume plays an equally crucial role in optimizing extraction yield. The evidence has been presented that increasing the solid-to-solvent ratio in various plant matrixes allows for an increase in total phenolic content (TPC). This occurs when the concentration gradient between the solid and the solvent increases, causing mass to be transferred. Nevertheless, it is common to choose higher ratios instead of lower ratios in order to save operational expenses and minimize the amount of solvent required (DiNardo et al., 2019).

In our study, as shown in figure 3.10, when the solid to solvent ratio increase from 1:30 to 1:50 g/ml, at constant methanol concentration (80%), the sample particles become more dispersed in the solvent, thereby augmenting the surface area of interaction between the two phases. This facilitates increased polyphenol exposure to the solvent; the former process involves dissolving and transferring the substances out of the sample matrix, thereby enhancing their extraction yield from 2.55 ± 0.05 to 3.75 mg GAE/g DW. Beyond 1:50 g/ml, the TPC amount decrease slightly to 3.48 ± 0.03 mg GAE/g DW when further raising the ratio from 1:50 to 1:70; too much volume can cause standing and dead wave zones, reducing microwave penetration. The volume of solvent must be adjusted to maximize energy absorption; the optimum solid/solvent ratio for microwave-assisted extraction was selected and set to be 1:50 g/ml.

- **Effect of microwave power**

High microwave power levels during phenolic compound extraction could occur to low recovery rates because of the degradation of thermo-labile compounds. Investigations have shown that the extraction efficiency of phenolic compounds from different vegetal matrixes initially rises toward a given limit, after which it decreases. The sample matrix is heated due to targeted contact with microwaves. This mechanism results in an increased dispersion of polyphenols within the plant matrix to the solvent (Ameer et al., 2017).

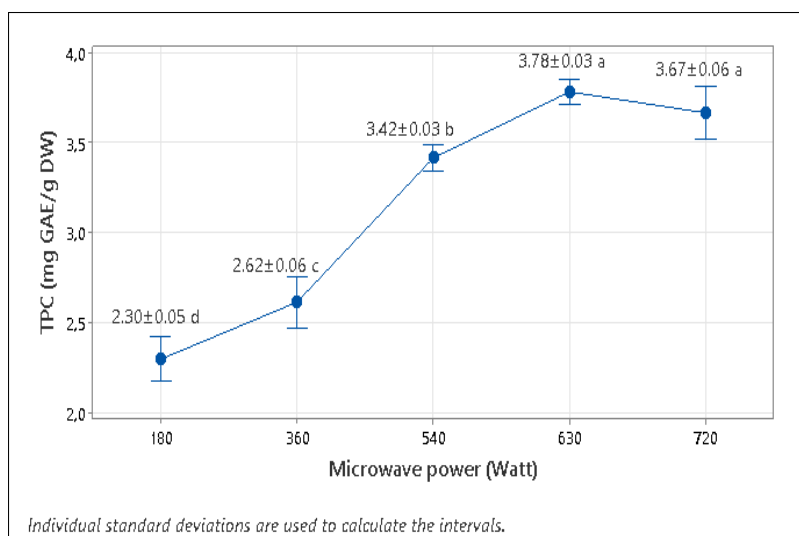


Figure 3.11: Effect of microwave power on TPC amount

As shown in figure 3.11, the level of total phenolic compounds (TPC) rises with microwave power up to 630 Watt, suggesting an increased release of phenolic compounds from the date palm powder matrix. However, higher power levels cause a decrease in TPC, suggesting possible degradation or modification of phenolic compounds. In summary, there is an optimal point of microwave power to maximize TPC (3.78 ± 0.03 mg GAE/g DW at 720 Watt), beyond which degradation of phenolic compounds may occur.

- **Effect of irradiation time**

Irradiation time has a significant influence on the yield of total phenolic compounds (TPC) extracted from date pulp powder (figure 3.12). The results show a linear increase in TPC up to 6 minutes of irradiation after which the TPC reaches threshold (3.82 ± 0.03 mg GAE/g DW), and even decreases slightly to 3.77 ± 0.06 mg GAE/g DW when boosting the extraction to 7 min. This suggests that longer irradiation may lead to more efficient extraction of phenolic compounds, but excessive exposure may lead to degradation of these compounds. Further study is needed to determine the optimal irradiation time to maximize the yield of phenolic compounds while preserving their integrity.

Controlling the extraction duration of MAE is crucial in order to minimize the potential for heat deterioration and oxidation (Wang et al., 2009).

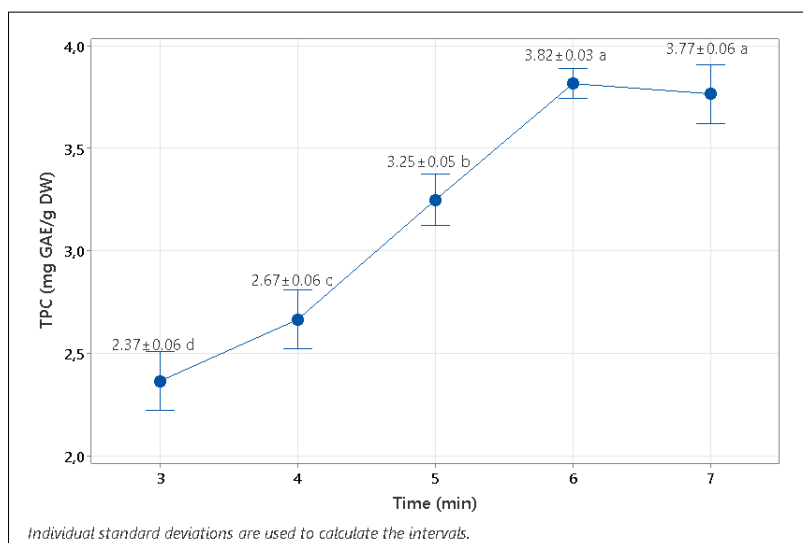


Figure 3.12: Effect of irradiation time on TPC amount

3.2.3.2. Optimization of TPC recovery by RSM

3.2.3.2.1. Model fitting

In order to maximize the extraction yield of phenolic compounds, BBD type experimental plan was implemented to evaluate the impact of major independent variables, including methanol concentration (X_1), microwave power (X_2), as well as the irradiation time (X_3). The results obtained were modelled through a second-degree polynomial, according to the response surface methodology “RSM”, thus accurately quantifying the interactions between these parameters and the total content of phenolic compounds expressed as mg gallic acid equivalent per gram dry matter (TPC, mg GAE/g DW). This model, validated by multiple regressions, highlights the individual effects and interactions of the variables, and serves as an optimization tool for maximizing TPC, as illustrated in equation (3.10):

$$\text{TPC (mg GAE/g DW)} = -14.09 + 0.0544 X_1 + 0.03096 X_2 + 1.240 X_3 + 0.000140 X_1^2 - 0.000020 X_2^2 - 0.1521 X_3^2 - 0.000123 X_1X_2 + 0.000646 X_1X_3 + 0.001296 X_2X_3 \quad (3.10)$$

3.2.3.2.2. BBD matrix and factors' main effect

The BBD response (Y) was determined by the yield of total phenolic compounds (%). Its matrix was carried out using three independent variables at three levels, with a total of 15 trials, 12 factorial points, and 3 central replicates, as shown in table 3.3:

Table 3.3: Box-Behnken matrix applied to the study of responses related to the total content in phenolic compounds extracted by MAE

Run Order	Methanol concentration (%)	Microwave power (Watts)	Irradiation time (min)	TPC (mg GAE/g DW) exp.	TPC (mg GAE/g DW) pred.	Residual
1	60	540	6	3.10	3.06	0.0347917
2	100	540	6	3.61	3.63	-0.0185417
3	60	720	6	4.26	4.24	0.0185417
4	100	720	6	3.89	3.92	-0.0347917
5	60	630	5	3.36	3.39	-0.0268750
6	100	630	5	3.51	3.49	0.0264583
7	60	630	7	3.90	3.93	-0.0264583
8	100	630	7	4.11	4.08	0.0268750
9	80	540	5	2.96	2.97	-0.0079167
10	80	720	5	3.48	3.47	0.0083333
11	80	540	7	3.30	3.30	-0.0083333
12	80	720	7	4.28	4.27	0.0079167
13	80	630	6	3.83	3.82	0.0133333
14	80	630	6	3.81	3.82	-0.0033333
15	80	630	6	3.81	3.82	-0.0100000

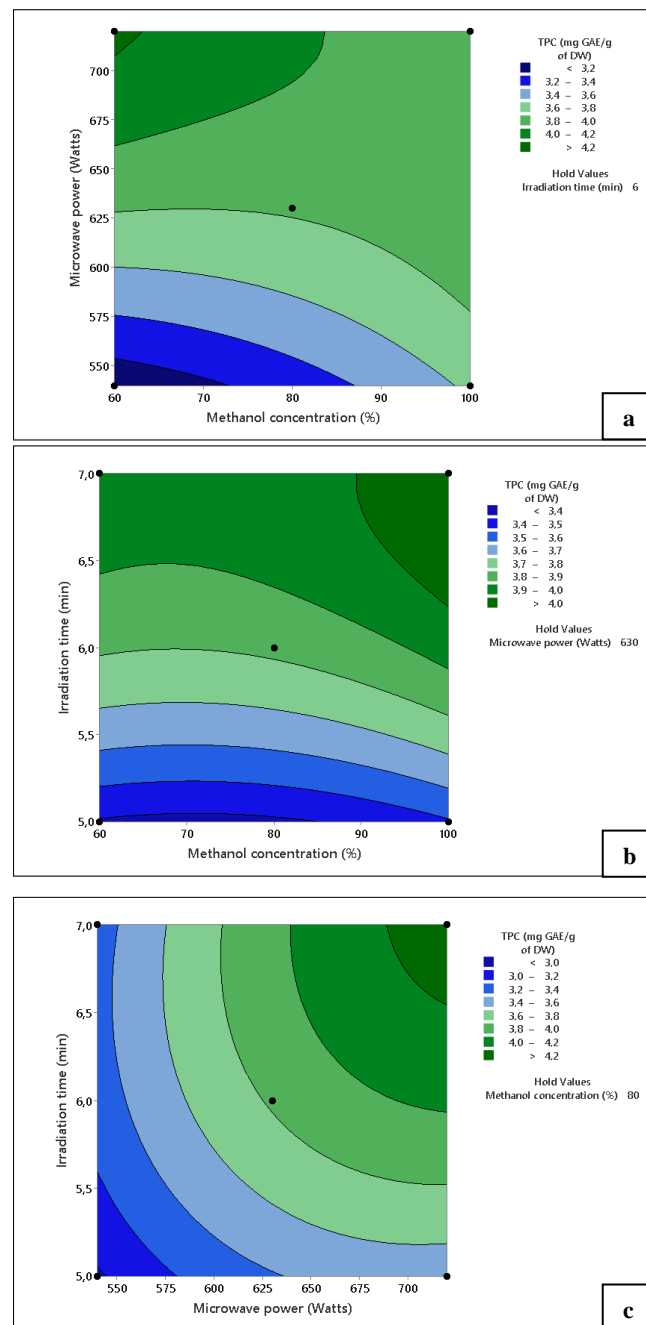


Figure 3.13: Contour Plot of TPC vs : Microwave power and Methanol concentration (a), Irradiation time and Methanol concentration (b), and Irradiation time and Microwave power (c)

The contour plot of Figure 3.13a displayed the integrated effect of microwave power and methanol concentration on the TPC yield from date pulp powder during a hold extraction time of 6 min. It is observed to be more strongly influenced by variations in the power of microwave irradiation as compared to changes in the amount of methanol used. Globally, TPC yield rise significant from 3.10 to 4.26 mg GAE/g DW by increasing the microwave power from 540 to 720 Watt as well as by increasing the methanol's concentration from 60 to 100%. On the other hand, by setting the microwave power to 630 watts around 5 minutes,

the total phenolic content (TPC) does not show a significant rise (from 3.36 to 3.51 mg GAE/g DW) even when the methanol concentration increases from 60 to 100%. However, by extending the extraction to 7 minutes, TPC jump to 4.11 (Figure 3.13 b). Finally, as show Figure 3.13c, holding the methanol at 80 %, the combined increase in microwave power (from 540 to 720 W) and irradiation time (from 5 to 7 minutes) significantly improved the yield of phenolic compounds, reaching a maximum of 4.28 mg GAE/g DW at 720 W and 7 min. This improvement can be explained by better disruption of cell structures and easier diffusion of compounds. Our results are in line with previous work demonstrating the significant impact of microwave-assisted extraction (MAE) operating parameters on total phenolic compound (TPC) yield. Indeed, the study by Alara et al. (2021) on *Carica papaya* leaves demonstrated that irradiation time, microwave power, as well as the ethanol concentration of the solvent, decisively influence extraction efficiency, with an optimum yield of 102.59 mg TPC/g MS obtained at 3 minutes irradiation, 420 W power, and 56% ethanol.

Despite the contribution of methanol concentration to the extraction yield of total phenolic compounds is only 1.44% (table 3.4), this does not necessarily mean that it has no significant effect and it still deserves attention in process optimization (P-value = 0.004), especially when combined with other variables to examine possible interaction; *i.e.*: As shown in figure 3.14, the Pareto chart demonstrate the factors that contribute most to the overall variability of the extraction of TPC using MAE at a significance level of $\alpha = 0.05$. Statistically, microwave power and irradiation time are the two most important factors affecting TPC (p-value = 0.00 and 0.001 respectively), followed by the interaction's effects of methanol concentration X Microwave power ($X_1 * X_2$) which still significant (p-value = 0.000). It can be explained by that in polar solvents such as solvent-water mixtures, higher microwave power enhances solvent penetration by disrupting hydrogen bonds and reducing surface tension (Tanruean et al., 2025).

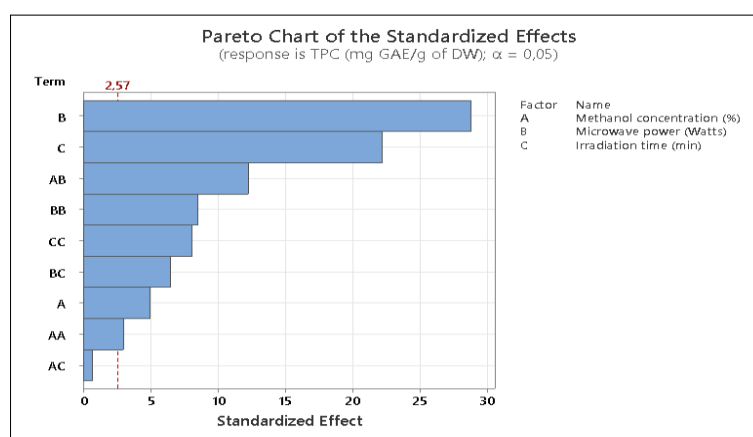


Figure 3.14. Pareto chart of the standardized effects of factors affecting TPC yield

3.2.3.2.3. Verification of the statistical models

In the analysis of the ANOVA results presented in table 3.4, we examine the relative contributions of different factors and their main effects on the extraction yield of total phenolic compounds, in order to illuminate the most influential factors as well as the complex relationships between them, thus offering key perspectives for the optimization of the extraction process. We also explore the implications of the results, highlighting the potential adjustments needed to improve extraction performance.

Table 3.4: Results of ANOVA for fitting models TPC yield (mg GAE/g DW) using microwave-assisted extraction (MAE)

Source	DF	Seq SS	Contribution (%)	Adj SS	Adj MS	F-Value	P-Value
Model	9	2.19193	99.70%	2.19193	0.24355	187.16	0.000
<i>Linear</i>	3	1.75161	79.68%	1.75161	0.58387	448.70	0.000
Methanol concentration (%)	1	0.03167	1.44%	0.03167	0.03167	24.34	0.004
Microwave power (Watts)	1	1.07678	48.98%	1.07678	1.07678	827.50	0.000
Irradiation time (min)	1	0.64317	29.26%	0.64317	0.64317	494.27	0.000
<i>Quadratic</i>	3	0.18940	8.62%	0.18940	0.06313	48.52	0.000
Methanol concentration (%) X Methanol concentration (%)	1	0.02277	1.04%	0.01151	0.01151	8.85	0.031
Microwave power (Watts) X Microwave power (Watts)	1	0.08123	3.69%	0.09403	0.09403	72.26	0.000
Irradiation time (min) X Irradiation time (min)	1	0.08540	3.88%	0.08540	0.08540	65.63	0.000
<i>2-Way Interaction</i>	3	0.25092	11.41%	0.25092	0.08364	64.28	0.000
Methanol concentration (%) X Microwave power (Watts)	1	0.19581	8.91%	0.19581	0.19581	150.48	0.000
Methanol concentration (%) X Irradiation time (min)	1	0.00067	0.03%	0.00067	0.00067	0.51	0.506
Microwave power (Watts) X Irradiation time (min)	1	0.05444	2.48%	0.05444	0.05444	41.84	0.001
Error	5	0.00651	0.30%	0.00651	0.00130		
Lack-of-Fit	3	0.00622	0.28%	0.00622	0.00207	14.35	0.066
Pure Error	2	0.00029	0.01%	0.00029	0.00014		
Total	14	2.19844	100.00%				
S	9	0.036					
R² (%)	3	99.70					
R² adj (%)	1	99.17					

First, the model as a whole is significant, with an F-Value of 187.16 and a P-value < 0.05, indicating that the model is statistically significant to explain the variation in extraction yield. Examining the various factors, Microwave power and irradiation time significantly influence extraction efficiency. A power of microwave irradiation contributes up to 48.98%,

and the irradiation time to 29.26%. These values indicate the relative importance of these two factors in the extraction process.

The error is also analyzed in ANOVA, showing an insignificant lack of fit (P-value = 0.066), this suggests that there are no sources of variation not explained by the model that which may indicate no adjustments needed to improve prediction of extraction yield. The coefficient of determination (R^2) quantifies the extent to which a model fits the data (Chicco et al., 2021). In our research, R^2 (%) and R^2 adjusted (%) indicate that the model explains respectively 99.70% and 99.17% of the observed variation in the extraction yield. This confirms the model's reliability to explain the variation in the data.

3.2.3.2.4. TPC yield Optimization

To verify the model's correctness, total phenolic compound of the date pulp powder was extracted under the recommended optimum conditions displayed in the optimization plot in figure 3.15. The TPC yield increased with increasing microwave power and irradiation time and it is maximized at their two highest ranges (720 watt and 7 min respectively). Nevertheless, the effect of methanol amount is more accentuated, and the extraction is maximized at the least concentration (60 %). The experimental TPC yield (4.56 ± 0.09 mg GAE/g DW) was close to the predicted results (4.47 mg GAE/g DW, with desirability $d = 1$).

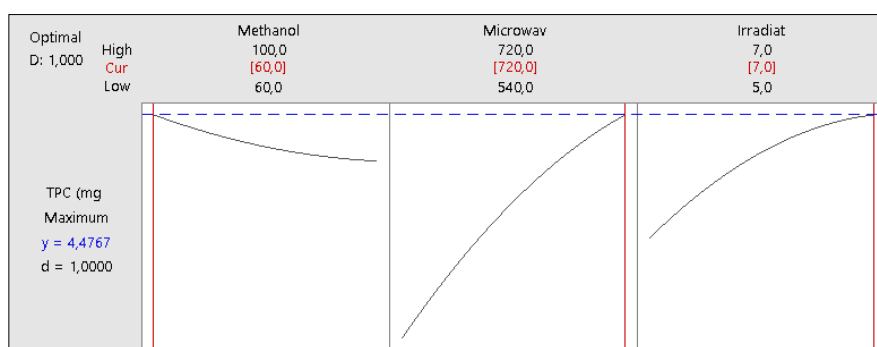


Figure 3.15. Optimization plot of TPC yield using MAE

3.2.3.3. Comparison between the extraction methods

Recovery of bioactive components like polyphenols from plant material requires extraction. Polyphenols may be extracted from dates using several techniques, such as traditional methods, including decoction, maceration or water bath, is both simple and cost-effective in terms of equipment. Its straightforward extraction process and its compatibility with commonly used solvents such as water, ethanol, methanol, acetone, chloroform, etc. make it widely employed in industry. Nevertheless, this approach is constrained by extended extraction durations, often lasting several hours, and elevated temperatures that may cause

degradation of some delicate polyphenols. Furthermore, it requires a substantial quantity of solvents, hence presenting environmental and safety concerns. The limitations may be overcome by using unconventional extraction techniques, such as MAE and UAE, each having unique benefits and drawbacks (Putnik et al., 2018).

Microwave irradiation considerably decreases extraction time to a few minutes while increasing efficiency via improved microwave penetration and even heat distribution. Additionally, it reduces the demand for solvents and energy. Nonetheless, this strategy needs the use of specialized equipment, which increases the initial cost, and there is a risk of thermal damage if temperature control is not accurate. Furthermore, it has a limited capacity to handle large quantities of raw materials (López-Salazar et al., 2023). Ultimately, the application of ultrasonic waves significantly decreases the extraction time to a few minutes or an hour. This is rendered feasible by the phenomena of ultrasonic cavitation, which efficiently breaks down plant cells and releases polyphenols. It uses solvents to a limited amount but also requires sophisticated and expensive equipment. The continuous presence of free radicals presents a threat to sensitive phenolic compounds, and processing performance is limited, comparable to microwave irradiation (Kumar et al., 2021). In overall, the approach used is determined by specific extraction objectives available resources, and operational limits.

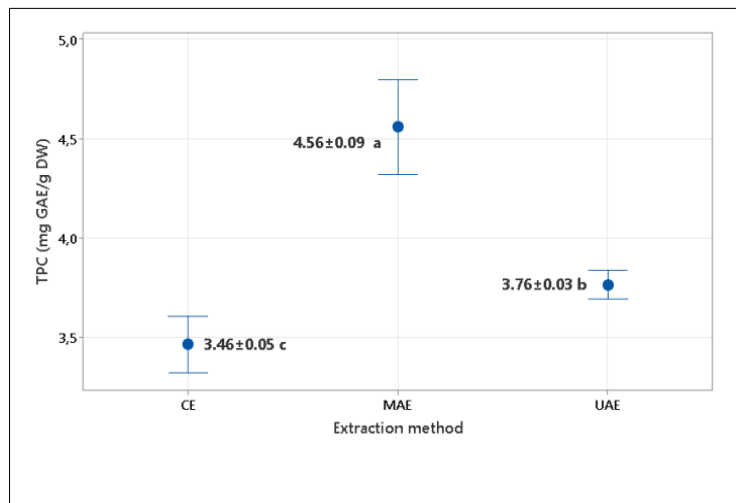


Figure 3.16. Comparison between MAE, UAE and CE methods

Applying MAE at optimal extraction conditions obtained, and after only 7 min of extraction, not only reduced the extraction time and the solvent's consumption, but also gave a higher yield (4.56 ± 0.09 mg GAE/g DW), followed by ultrasonic assisted extraction (UAE) and maceration (CE), as shown in individual value plot of TPC in figure 3.16. This emphasizes the significance of selecting the extraction procedure in order to optimize the retrieval

of bioactive chemicals from dates that have low commercial value. The obtained TPC values were compared to those reported in the literature, revealing similarities to certain studies and differences to others, essentially attributable to extraction conditions, irrespective of variety.

In Biglari et al. (2008), the maceration of the pulp of *Kharak* (Dry dates) in a methanol/water mixture (80:20) at 20°C for 5 hours extracted only 1.41 ± 0.04 mg GAE/g DW of TPC. Similarly, Tassoult et al. (2021), using a methanol/water ratio of 65:35, obtained modest contents ranging from 1.33 ± 0.08 to 2.52 ± 0.03 mg GAE/g DW, depending on the variety. This low yield can be explained by the slow solvent penetration into plant cells, leading to an incomplete solubilization of bound phenolic compounds.

As for Sedraoui et al. (2020), applying ultra-high pressure assisted extraction, this method uses extremely high pressures (often in excess of 100 MPa) to disrupt cellular structures and facilitate extraction of secondary metabolites. Despite this, the CPT obtained was only 2.57 ± 0.02 mg GAE/g DW, which remains modest compared with our study. This average performance could be due to sub-optimal time or temperature, or to interferences linked to the nature of the solvent or sample preparation. On the other side, in the study by Djaoud et al (2020), applying MAE for *Degla Beida* variety, the use of a methanol/water mixture (60:40) at 700 W achieved a yield of 2.12 ± 0.07 mg GAE/g DW, which is still lower than our result. Several possible reasons for this intermediate performance; as temperature too high locally, leading to possible thermal degradation of phenolic compounds, duration or power not optimized for the type of matrix under consideration.

3.2.4. UPLC-ESI-MS/MS analysis of Phenolic-Rich Date Extract (PRDE)

UPLC-ESI-MS/MS analysis of the phenolic profile of the methanolic extract of date powder obtained by MAE under optimized conditions revealed a notable diversity of bioactive compounds. This study, based on the combined use of the chromatogram (Figure 3.17), chromatographic and spectral characterization of compounds (Table 3.5) and chemical classification (Table 3.6), highlights the richness, relative abundance and biochemical nature of the metabolites identified.

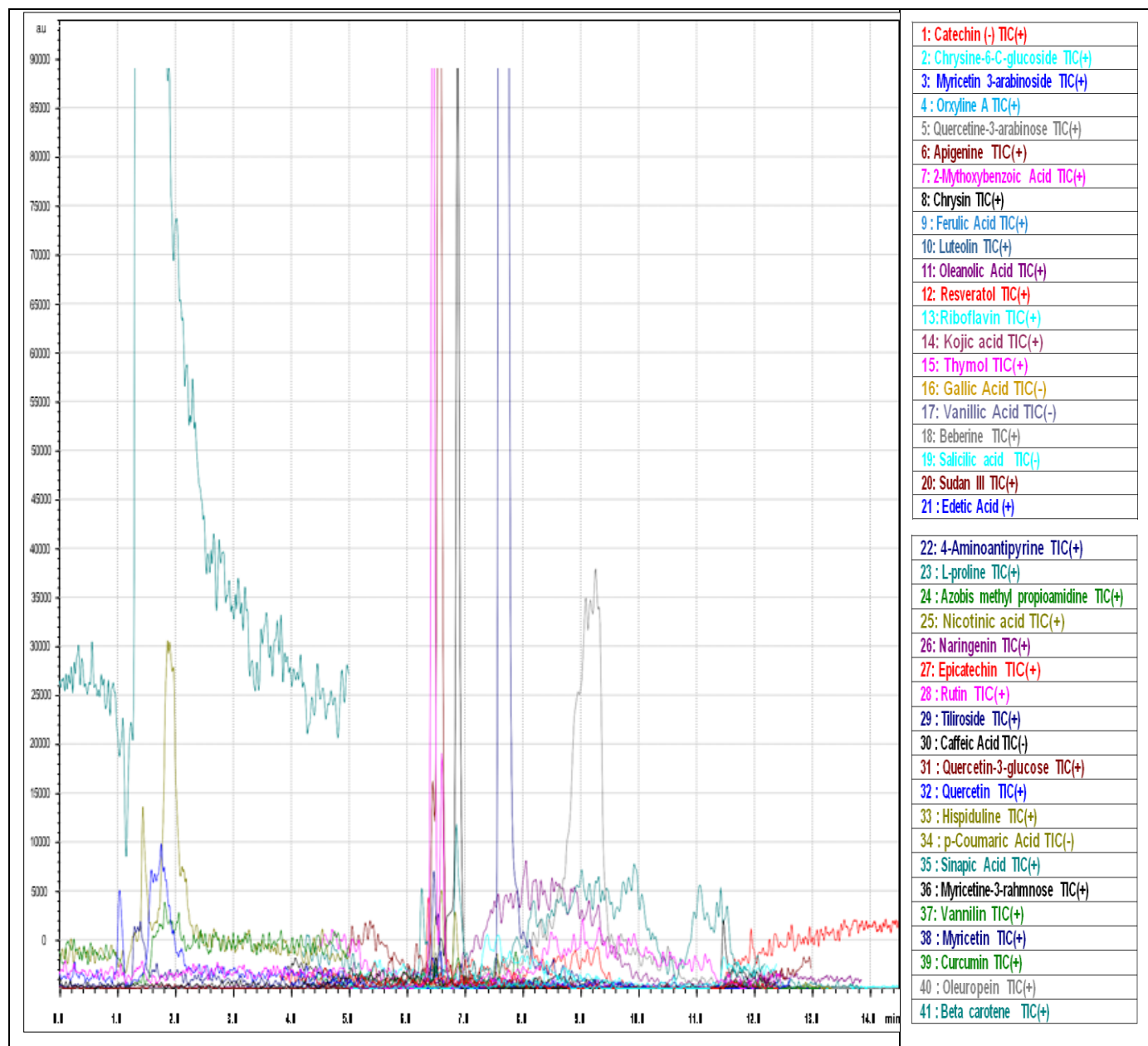


Figure 3.17: UPLC-ESI-MS/MS chromatogram of the methanolic date extract obtained by MAE

(Rt: from 0 to 14 min)

Table 3.5: Compound identification and signal intensity detected by UPLC-ESI-MS/MS of the optimized phenolic date extract obtained by MAE

ID	Rt (min)	Name	Formula	ESI charge	CE* (v)	transition m/z	Area	Height
1	1.284	4-Aminoantipyrine hydrochloride	C ₁₁ H ₁₄ ClN ₃ O	+	-21	204.1000>55.9000	6637	1582
2	1.363	L-Proline	C ₅ H ₉ NO ₂	+	-17	116.1000>69.9000	49601592	10155904
3	1.814	Azobis methyl propioamidine	C ₈ H ₂₀ Cl ₂ N ₆	+	-8	271.9000>231.2000	135314	6924
4	1.900	Nicotinic acid	C ₆ H ₅ NO ₂	+	-23	123.9000>79.8500	179892	13136
5	6.145	Naringenin	C ₁₅ H ₁₂ O ₅	+	-43	273.0500>153.0000	10100	960
6	6.366	Epicatechin	C ₁₅ H ₁₄ O ₆	+	-15	290.8000>139.1500	24329	5237
7	6.448	Rutin	C ₂₇ H ₃₀ O ₁₆	+	-10	611.0000>303.1000	362396	93372

Table 3.5: Compound identification and signal intensity detected by UPLC-ESI-MS/MS of the optimized phenolic date extract obtained by MAE (Continued)

ID	Rt (min)	Name	Formula	ESI charge	CE* (v)	transition m/z	Area	Height
8	6.465	Tiliroside	C ₃₀ H ₂₆ O ₁₃	+	-18	595.0000>286.9500	77047	11447
9	6.498	Caffeic Acid	C ₉ H ₈ O ₄	-	34	179.1500>135.0000	7318	2068
10	6.559	Quercetine-3-glucoside	C ₂₁ H ₁₉ O ₁₂	+	-18	465.1000>303.0500	445693	101649
11	6.576	Quercetine	C ₁₅ H ₁₀ O ₇	+	-52	303.0500>153.1000	8274	1506
12	6.599	Hispiduline	C ₁₆ H ₁₂ O ₆	+	-10	301.1000>268.8000	55275	9532
13	6.834	p-Coumaric Acid	C ₉ H ₈ O ₃	-	28	163.0500>118.9500	34907	7075
14	6.854	Sinapic Acid	C ₁₁ H ₁₂ O ₅	+	-23	225.0000>175.0500	45039	8379
15	6.877	Myricetine-3-rhamnose	C ₂₇ H ₃₀ O ₁₇	+	-44	465.0000>54.8500	554141	100235
16	6.889	Vannilin	C ₈ H ₈ O ₃	-	-15	153.0500>64.7500	30421	2147
17	7.643	Myricetin	C ₁₅ H ₁₀ O ₈	+	-20	318.5000>256.0500	7207169	1347685
18	7.880	Curcumin	C ₂₁ H ₂₀ O ₆	+	-20	368.9000>177.0500	16826	3310
19	9.261	Oleuropein	C ₂₅ H ₃₂ O ₁₃	+	-15	540.5000>523.4000	544957	16071
20	11.045	Beta-carotene	C ₄₀ H ₅₆	+	-19	537.1000>280.9500	107062	5288

CE: collision energies in volts; ESI: ElectroSpray Ionisation

UPLC-ESI-MS/MS analysis of the methanol extract of dates obtained by microwave-assisted extraction (MAE) reveals a remarkable richness in phenolic compounds and bioactive metabolites (table 3.5), confirming the effectiveness of the optimized extraction conditions. The chromatogram reveals a clear separation of compounds over a relatively short retention window (0–14 min), reflecting good chromatographic performance and adequate compatibility between the mobile phase and the analyzed matrix. The simultaneous presence of major flavonoids (myricetin, quercetin, and their glycosylated derivatives), phenolic acids (caffeic, p-coumaric, sinapic), and compounds with high functional value such as oleuropein and curcumin highlights the extract's high antioxidant and biofunctional potential.

The particularly high abundance of L-proline suggests that date extract obtained by MAE is an interesting source of osmoregulatory compounds involved in the cellular stress response (Krishnan et al., 2025). Furthermore, the differences in signal intensity observed between compounds can be attributed to variations in intrinsic concentration, ESI ionization efficiency, and molecular stability (Jiang et al., 2024). Furthermore, as confirmed by Srivastava et al. (2025), the absence of detection of certain targeted compounds can be explained by concentrations below the detection threshold or by insufficient ionization, a phenomenon frequently reported in mass spectrometry coupled with ESI. These results confirm the effectiveness of MAE for the selective extraction of phenolic compounds from dates and their functional valorization.

The detailed chemical classification of the identified compounds is summarized in the table 3.6 below, according to a typology based on their structure and biosynthetic part.

Table 3.6: Classification of compounds of the phenolic extract by chemical and class and sub-class

Compound name	Class and Sub-class
Flavonoids (flavonols, flavones) (18 compounds)	
Myricetin	Flavonol
Myricetin 3-arabinoside	Flavonol O-glycoside
Myricetine-3-rhamnose	Flavonol O-glycoside
Quercetine	Flavonol
Quercetine-3-glucoside	Flavonol O-glycoside
Quercetine-3- arabinose	Flavonol O-glycoside
Rutin	Flavonol diglycoside (rutinoside)
Tiliroside	Esterified Flavonol
Hispiduline	Methoxylated flavone
Curcumin	Diarylheptanoid (close to flavonoid)
Naringenin	Flavanone
Epicatechin	Flavanol (catechol)
Catechine(-)	Flavanol
Chrysin	Flavone
Luteolin	Flavone
Apigénine	Flavone
Orxyline A	Methoxylated flavone
Chrysin-6-C-glucoside	Flavone C-glycoside
Phenolic acids (9 compounds)	
Caffeic Acid	Hydroxylated cinnamic acid
Ferulic Acid	Methoxylated cinnamic acid
Sinapic Acid	Methoxylated cinnamic acid
p-Coumaric Acid	cinnamic acid
Gallic Acid	Trihydroxybenzoic acid
Vanillic Acid	Methoxylated benzoic acid
Salicilic acid	Ortho-hydroxybenzoic acid
Vannilin	phenolic aldehyde
2- mythoxybenzoic Acid	Methoxylated benzoic acid (anistic)
Iridoid compounds and complex phenols	
Oleuropein	Phenolic glycosylated secoiridoid
Carotenoids and isoprenoids	
Beta-carotene	Tetranepen (carotenoid)
Amino acids and nitrogen derivatives	
L-Proline	Cyclic amino acid
Nicotinic acid	Pyridine Derivative / Vitamin B3
Beberine	Isoquinolein alkaloid
4-Aminoantipyrine hydrochloride	Pyrazole derivative/ Antipyretic
Azobis methyl propioamidine	Azoamidine compound
Sudan III	Azo derivative/ dye
Edetic Acid	Chelating polycarboxylic amino acid
Riboflavin	Vitamin B2 (flavin)
Simple phenols various	
Thymol	Phenolic monoterpene
Kojic acid	Hydroxylated lactone (fungal phenolic)

The typical BPC chromatogram shows numerous peaks numbered according to elution order, with a marked concentration of compounds between 6 and 8 minutes retention, reflecting

a predominance of an intermediate polarity of the dominant compounds, notably glycosylated flavonoids and phenolic acids. These compounds were identified by comparing their UV spectra and MS/MS spectrometric signatures with data reported in the specialized literature. Of the forty or so compounds detected, only twenty generated quantifiable signals (area > 0), underlining their significant contribution to the bioactive and antioxidant potential of the extract analyzed.

Analysis of the compounds identified by UPLC-ESI-MS/MS reveals a structured distribution of R_t , which faithfully reflects the physicochemical characteristics of the molecules. Indeed, the R_t values obtained under the experimental conditions applied (probably under an increasing elution gradient in the organic phase) reflect the differential interaction of compounds with the hydrophobic stationary phase (C18 column) as a function of their polarity and molecular weight. Three distinct groups emerge from this distribution:

1) Highly polar, low-molecular-weight compounds ($R_t < 2$ min):

As water-soluble compounds, generally small in size and rich in polar functions (acids, amines, nitrogen heterocycles, see table 3.6), are eluted at the very start of analysis. These include : L-proline ($R_t = 1.363$ min, $M = 115$ g/mol), this compound stands out with an exceptionally high area (49601592), which could reflect a high content of free amino acids in the extract. According to the statement of Batista-Silva et al. (2019), this probably linked to an adaptive response of the plant to stress or intensive metabolic activities. Also, we find 4-aminoantipyrine hydrochloride ($R_t = 1.284$ min); azobis methyl propioamidine ($R_t = 1.814$ min); and nicotinic acid ($R_t = 1.9$ min).

These low retention times reveal a marked affinity for the aqueous mobile phase, limiting interaction with the stationary phase, as reported by Jandera & Hájek (2020). This behavior is typical of highly polar compounds, whose elution is favored from the very first minutes. It should be noted that these molecules, although accessory to a strict phenolic profile, reflect the metabolic richness of our phenolic date extract, particularly in terms of endogenous nitrogen compounds, such as certain free amino acids or secondary nitrogen metabolites, frequently reported in the biochemical composition of date palm (*Phoenix dactylifera*) (Hadrami et al. , 2011).

2) Compounds of intermediate polarity and moderate molecular weight ($R_t \approx 6 - 8$ min):

The majority of phenolic compounds detected fall within this chromatographic window, which constitutes a remarkable structural signature. These are mainly glycosylated flavonoids

(see table 3.6, e.g. quercetin-3-glucoside, $R_t = 6.559$ min, area = 445693). These glycosylated derivatives are not only characteristic of plant flavonols, but are also associated with superior bioavailability compared to aglycone forms, a phenomenon well documented by Olthof et al. (2000) in their work on the intestinal absorption of dietary flavonoids. Also, the aglycone flavonoids (e.g. quercetin, $R_t = 6.576$ min); Substituted phenolic acids (e.g. sinapic acid, $R_t=6.854$ min; p-coumaric acid, $R_t = 6.834$ min); Curcumin ($R_t = 7.880$ min); and Myricetin ($R_t = 7.643$ min, and area = 7207169), a major flavonol, known for its antioxidant, anti-inflammatory and neuroprotective activities (Pluta et al., 2021). The concentration of these compounds in the same R_t range reflects intermediate polarity, linked to the presence of hydroxylated aromatic rings, glycosidic residues or conjugated carbon chains (Sakurai et al., 1976). A moderate molecular weight (250-600 Da) generally induces an intermediate retention time, associated with increased interaction between larger molecules and the stationary phase (Jandera & Janás, 2017).

3) *Low-polarity compounds ($R_t > 9$ min)*

Compounds with retention times of over 9 minutes, such as Oleuropein (see table 3.6), a glycosylated secoiridoid representing one of the major phytomolecular markers of *Olea europaea*, stands out for its esterified aromatic structure, high molecular weight ($M = 540$ Da) and prolonged retention time ($R_t = 9.261$ min, area = 544957), characteristic of a strongly hydrophobic compound. Moreover, its antioxidant, anti-inflammatory and metabolic properties make it an essential bioactive lipid in edible oils, contributing to their vasculoprotective effects (Rey et al., 2022).

Beta-carotene ($R_t = 11.045$ min, $M = 536$ Da) features a high retention time, indicative of its marked structural lipophilicity and strong affinity for the stationary phase in reverse-phase liquid chromatography (RP-HPLC). In this context, the low polarity explains their prolonged interaction with the apolar stationary phase, making it necessary to enrich the mobile phase with organic solvents such as methanol or acetonitrile to facilitate their elution. With that in mind, a high retention time is a reliable indicator of structural hydrophobicity, directly related to parameters such as lipophilicity ($\log P$), molecular complexity and molecular volume. This structure-retention relationship has been clearly established by Liang and Lian (2015), who highlight the robustness of RP-HPLC as the experimental method of choice for quantifying the lipophilicity of bioactive compounds.

To overcome the analytical limitations associated with the co-detection of water- and fat-soluble compounds, Melfi et al. (2018) have developed a dual-injection RP-HPLC method,

using two analyte polarity-specific mobile phases and differentiated UV detection (260 nm for vitamins, 450 nm for carotenoids). Analysis is carried out under light-protected conditions, using suitable organic solvents (e.g. methanol) to maintain beta-carotene stability. This strategy enabled accurate and reproducible simultaneous analysis, with recoveries >90% and reduced analytical variability (RSD <5%), underlining the relevance of differentiated chromatographic approaches for complex matrices.

It is important to mention also that the high levels of nicotinic acid (179892) and beta-carotene (107062) reflect a mixed metabolic component in our date extract, where water-soluble molecules (vitamins) and lipophilic molecules (carotenoids) intersect.

On this basis, and as studied by Benhadji (2023), chromatographic structuring reinforces the robustness of the UPLC-ESI-MS/MS analysis used, ensuring optimum separation of chemical families while enabling rational interpretation of the metabolic complexity of the mixture studied.

In order to better situate the results obtained, this section proposes a comparative discussion with other work using HPLC for the identification and quantification of phenolic compounds extracted from date palm.

In the present work and that of Djaoud (2020), the MAE method was used, recognized for its effectiveness in improving the yield of thermo-extracted compounds. However, our study uses a 60% methanolic solvent, while Djaoud (2020), uses 50% ethanol, which can modulate the polarity of the extracted compounds. In contrast, Ouamnina et al. (2024) use room temperature maceration with a 60% hydro-ethanolic solvent, a less aggressive but often less efficient method for the extraction of cell wall bound metabolites. These results are consistent with those of Xiang et al. (2024), who point out that the extraction method as well as the type and concentration of solvents significantly influence the composition and structure of the extracted phenolic compounds, by acting on the polarity of the medium and the affinity towards the target molecules.

Analytically, the present study is based on a high sensitivity UPLC-ESI-MS/MS system (Shimadzu 8040), capable of detecting compounds at very low concentrations and generating specific m/z transitions. In comparison, Djaoud (2020) uses a HPLC system coupled to an ion trap, less sensitive but effective for the identification of certain classes of compounds. Ouamnina et al. (2024) limit themselves to UV-VIS detection at 280 nm, which complicates the fine differentiation of complex isomers or glycosides. In this context, the study of Zhao et al. (2018) discusses the advantages and disadvantages of different analytical techniques, such as HPLC, UPLC, LC-MS/MS, for the identification and quantification of phenolic

compounds in plant extracts, emphasizing that the choice of method influences sensitivity, selectivity and ability to detect certain compounds.

In the present study, the Algerian variety “*Mech Degla*” was found to be particularly rich in reducing sugars and bioactive phenolic compounds. Using a highly sensitive UPLC-ESI-MS/MS system, over forty compounds were identified, including quercetin-3-glucoside, myricetin-3-rhamnose and beta-carotene, highlighting both the analytical efficiency of the method and the antioxidant potential of this variety. For their part, Djaoud et al (2020) highlighted a similar richness in “*Degla Beida*”, with the identification of several families of compounds such as lignans, flavonols, carotenoids and proanthocyanidins. In comparison, Moroccan dates analyzed by Ouamnina et al. (2024), although extracted by a different method, show a more restricted phenolic diversity, with only twelve compounds detected, mainly classical (catechin, gallic, caffeic, ferulic and vanillic acids). These variations in phenolic compound composition and concentration between the different studies can be attributed to several factors, including environmental conditions as well as the varietal specificities of the dates studied, as also confirmed by the work of Alkhudaydi et al. (2025).

Our study stands out for the richness of its chromatographic profile, notably the dominant presence of myricetin (signal of 7.2 million), followed by quercetin-3-glucoside, myricetin-3-rhamnose, oleuropein and other complex flavonols. These compounds, well known for their antioxidant effects, were not detected or only detected in trace amounts in the other studies. The combination of MAE and UPLC-MS/MS therefore enabled more sensitive quantification and more efficient separation.

In Djaoud (2020), additional families such as dimeric and trimeric procyanidins, apocarotenoid carotenoids and saponins are highlighted. These compounds are not specifically reported in our study, probably due to detection thresholds or analytical choices. In contrast, Ouamnina et al. (2024) reports only the most common compounds, such as quercetin, gallic acid and catechin, in low to moderate concentrations, highlighting an analytical limitation. These results corroborate the observations of Alam (2024), who compiles similar data from decades of research into phenolic extraction from dates.

Alam' team workers synthesis shows a predominance of the following compounds in the majority of varieties studied worldwide: quercetin, ferulic acid, caffeic acid, catechin, epicatechin, luteolin and rutin. Our results confirms this trend, while also providing better fine identification of certain rarely detailed glycosides (quercetin-3-arabinose, glycosylated myricetin).

This methodological combination of microwave-assisted extraction “MAE” and UPLC-ESI-MS/MS analysis not only enabled more efficient separation of compounds, but also more sensitive quantification, demonstrating a significant advance that reinforces the relevance of this integrated approach to the study of phenolic extracts.

3.2.5. Antioxidant activity *in vitro* of the phenolic extract

Under oxidative stress, cells produce more reactive oxygen species (ROS), such as hydroxyl radicals, often exceeding the protective capacity of non-enzymatic antioxidants such as lycopene, ascorbic acid and quercetin. Insufficiency of antioxidants, which inhibit the activity of reactive free radicals, increases the progress of degenerative disorders, such as inflammatory and cardiovascular diseases. One potential remedy for that issue is to include antioxidant compounds derived from natural plant sources into a dietary supplement (Krishnaiah et al., 2011). Recent studies have suggested that the consumption of antioxidant-rich foods is negatively correlated with the prevalence of human diseases (Jideani et al., 2021). However, synthetic antioxidants as phenolic derivatives such as those from toluene and anisole substituted by hydroxyl and alkyl groups often referred to by their acronyms BHT and BHA, used in the agro-food industry, may cause liver damage and cancer (Ren et al., 2025). This has boosted interest in natural antioxidants.

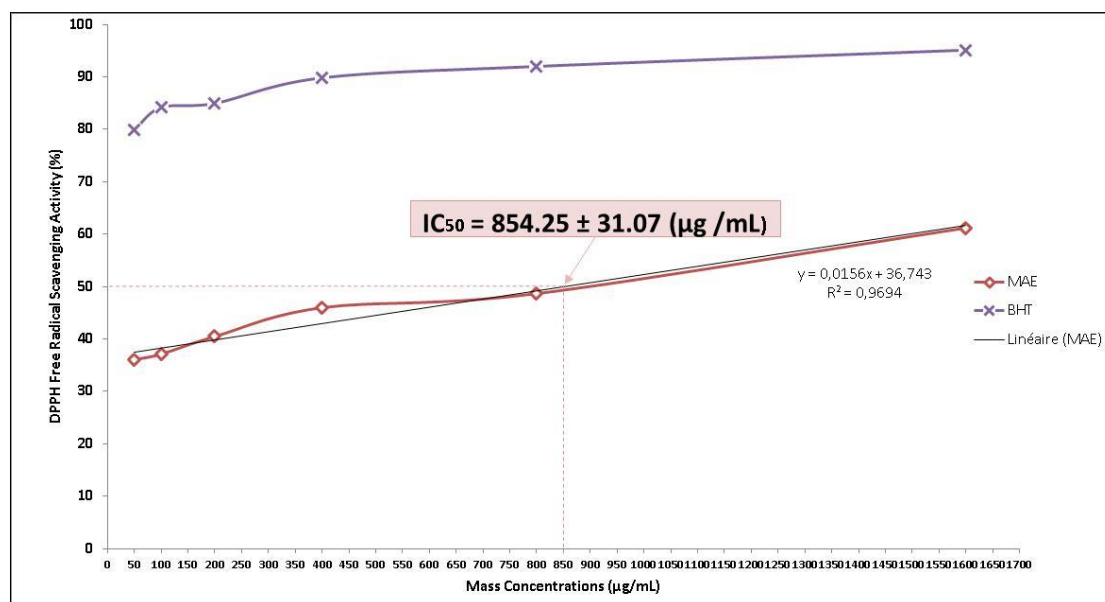


Figure 3.18: DPPH Free radical scavenging activity of the obtained extract by MAE

The presence of the phenolic group gives these compounds a strong antioxidant capacity, in particular to neutralize the radical DPPH. Our optimized DPAE presented an IC_{50} of $854.25 \pm 31.07 \mu\text{g/mL}$ of methanolic extract (Figure 3.18), whereas, the IC_{50} of

ascorbic acid is 6.1 $\mu\text{g/mL}$, as per Nariya et al. (2013). This suggests that ascorbic acid is approximately 140 times more effective at neutralizing free radicals, which requires a significantly higher concentration of our PRDE for achieving a comparable antioxidant effect. The most optimal process for the targeted extraction of bioactive compounds from date pulp is microwave irradiation, as these results prove.

Analysis of the antioxidant activity of the methanolic extract of the *Mech Degla* variety, obtained by MAE, revealed an IC_{50} value of $854.25 \pm 31.07 \mu\text{g/mL}$, reflecting moderate activity. In comparison, Messadi et al (2023), using the same variety with conventional aqueous and methanolic extractions, report much higher values (4800 and 14000 $\mu\text{g/mL}$ respectively), highlighting the superior efficiency of MAE in extracting antioxidant compounds. On the other hand, lower IC_{50} were observed by Ali Haimoud et al. (2016) (206-380 $\mu\text{g/mL}$) on other Algerian varieties, as well as by Abdelbaky et al. (2023) (352-504 $\mu\text{g/mL}$) on Egyptian varieties, confirming the importance of genotype and extraction method in the variability of antioxidant activity. These results demonstrate that, although *Mech Degla* is relatively low in soluble phenolic compounds, optimizing extraction conditions, in particular via MAE, can significantly improve its antioxidant yield.

3.3 Conclusion

The morphometric, physicochemical, and phytochemical attributes of the "*Mech-Degla*" date fruit were highlighting their suitability for various food and industrial applications. The findings indicated that the "*Mech-Degla*" dates are abundant in vital energy molecules such as sugars, highlighting their suitability for various food and industrial applications; furthermore, the total phenolic content was quantified, underscoring the fruit's potential as an antioxidant compound source, suggesting its use as a natural antioxidant.

The extraction of the phenolic chemicals was optimized using MAE in conjunction with RSM. This method was found to significantly enhance the yield of phenolic compounds compared to conventional extraction techniques. The phenolic extraction yields obtained through MAE were also compared with those produced using UAE and CE techniques, with MAE demonstrating superior efficiency.

Upon UPLC-ESI-MS/MS phenolic profiling of the optimized extract, we founded that retention times in relation to the chemical nature of the compounds reveals a clear hierarchy in the phyto-compound profile analyzed: First, polar and light compounds are eluted early, in a predominantly aqueous mobile phase. Then, structured phenolic compounds (flavonoids, hydroxycinnamic acids) are eluted in an intermediate window, reflecting their

hydrophilic/lipophilic balance. In final, non-polar, high-molecular-weight compounds elute late, requiring more advanced organic conditions. Finally, the *in vitro* antioxidant activity of the optimized phenolic extract demonstrated a remarkable ability to trap free radicals, underlining its potential as a natural antioxidant for various applications.

These findings highlight the importance of maximizing the use of natural resources while promoting sustainable and economic practices, by open up several avenues for further research. Firstly, a biological validation of the extracts, combined with an absolute quantification of major compounds, would consolidate their nutraceutical potential. Also, exploring other varieties or parts of the date plant, as well as studying the stability of compounds during storage or processing, would provide a better understanding of their behavior in real-life conditions. In addition, the adoption of non-targeted metabolomics approaches via techniques such as NMR or LC-QToF could enrich this molecular mapping and reveal additional biomarkers of interest. Finally, encapsulation of active extracts appears to be a promising way of improving stability and bioavailability for functional applications.

Chapter 4

Optimization of the date pulp aqueous extract production, and full characterization

The extracting the quasi-totality of soluble constituents from the pulp of *Phoenix dactylifera* L. is a significant barrier for their valorization in the date fruit sector. Conventional water extraction procedures, however, exhibit limitations regarding efficiency and processing duration. The main goal of this study is to enhance the extraction recovery (ER) of total soluble matter from date pulp while incorporating a comprehensive evaluation of the resultant date pulp extract. This study aims to examine several extraction methods, expanding upon prior studies. The optimization of an extraction process must extend beyond the examination of individual factor impacts; it is essential to investigate the interactions among parameters and the quadratic effects that impact the total response. These intricate relationships can only be accurately evaluated by a statistical methodology, such as the Box-Behnken design (BBD). We are evaluating the impact of three extraction methods—water bath, microwave, and ultrasound—on extraction recovery, as well as on the functional qualities, biochemical features, and antioxidant and antibacterial activities of each optimized extract. This integrated method seeks to enhance the efficiency of the extraction process while ensuring the production of natural date pulp extracts with appropriate functional and nutritional attributes.

4.1. Materials and methods

4.1.1. Plant material

We chose the “*Mech Degla*” date palm fruit cultivar (*Phoenix dactylifera* L.) from the local market in Biskra, which is located in the southeast region of Algeria. The dates were collected when they were at the T'mar stage of maturity. The fresh pulp was cleaned and pitted, and then it was dried in a vented oven (Memmert UN 260, GmbH, Schwabach, Germany) at a temperature of 40°C until it reached 18.31 kilograms, which is equivalent to 91.55 % of the prior fresh weight. The pulp that had been dried, which had 4.98% ± 0.02% moisture content of its initial weight after drying, was ground in order to enhance the interface for exchange and make

extraction easier. After that, the pulp was sieved to a size of 200 μm . The date powder that was obtained was kept at a temperature of $-18\text{ }^{\circ}\text{C}$ until it was utilized.

4.1.2. Chemical reagents

It was from Merck Millipore in Burlington, Massachusetts, USA, that we obtained phenolphthalein, phenol, 3,5-dinitrosalicylic acid, quercetin, aluminum trichloride (anhydrous), and potassium sodium tetrahydrate, as well as 96% sulfuric acid. Ethanol and acetone were purchased from Scharlau (Barcelona, Spain). Folin-Ciocalteu reagent, gallic acid, sodium carbonate, sodium hydroxide methanol, copper sulfate pentahydrate, potassium sulfate, boric acid, methylene blue, methyl red, hydrochloric acid, butylated-hydroxytoluene (BHT), 2,2-diphenyl-1-picrylhydrazyl radical (DPPH), phenyl- β -D-glucoside, hydroxylamine chloride in pyridine, hexamethyldisilazane (HMDS), trifluoroacetic acid (TFA), heptane, glucose, fructose, sucrose, caffeic acid, o-coumaric acid, ferulic acid, and sinapic acid, from Sigma Chemical Co (St. Louis, USA). Analytical grade chemicals and reagents were used in all the analysis.

4.1.3. Extraction recovery determination

For the purpose of determining the ER of all DPAE samples, we utilized the equation (4.1) that was described by Ganbi (2012):

$$\text{ER}(\%) = \left(\frac{W_{\text{extract}} \times \% \text{ of TSS}_{\text{extract}}}{W_{\text{pulp}}} \right) \times 100 \quad (4.1)$$

In which: ER represents the extraction recovery of total soluble solids expressed as a percentage, W_{extract} represents the weight of the DPAE in grams, and % of $\text{TSS}_{\text{extract}}$ represents the total soluble solids content in the DPAE represented as a percentage of sucrose according to fresh weight (% FW).

4.1.4. Preliminary essays

Using a one-factor experiment, preliminary essays established the optimal range values, coded as inferior (-1), median (0), and superior ($+1$) levels of these factors, as presented in Table 4.1. The preliminary «one-factor» tests consist of evaluating the influence of each parameter on ER individually, while simultaneously maintaining the other two parameters constant, for the three extraction methods.

4.1.4.1. For WAE

- S/L Ratio (g/mL) (variable), with Temperature = 95 °C (constant), and Time = 30 min (constant): ER values are 34.36, 34.42, and 34.40 %, for 1/7, 1/5, and 1/3 g/mL, respectively (figure 4.1):

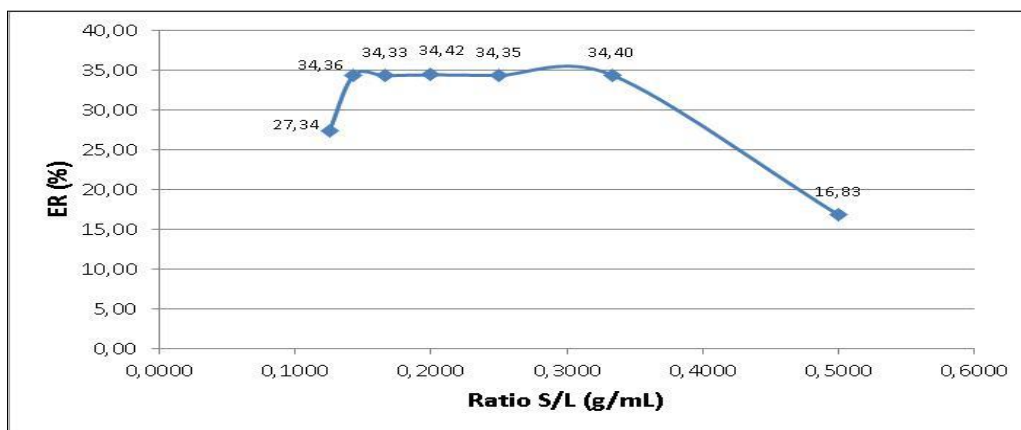


Figure 4.1. Variation of ER in function of Ratio S/L, applying WAE

- Temperature (T°C) (variable) , with Ratio S/L = 1/5 g/mL (constant) , and Time = 30 min (constant): ER values are 42.93, 44.81, and 43.83 %, for 70, 75, and 80 °C, respectively (figure 4.2):

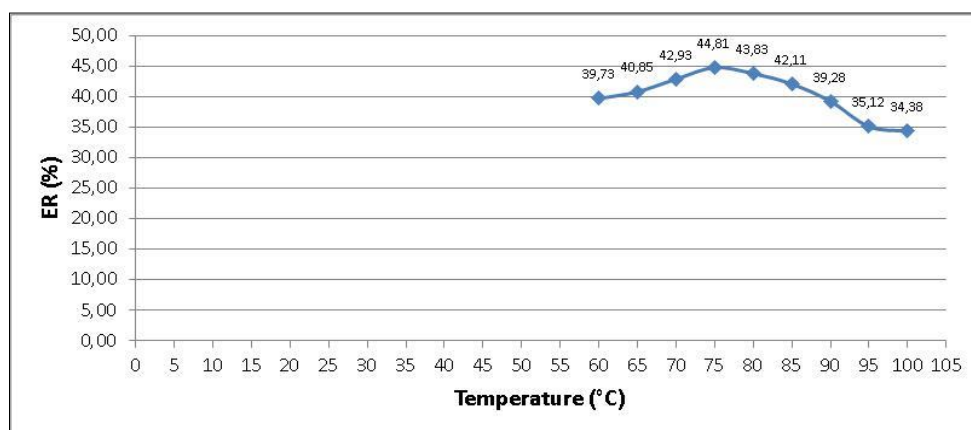


Figure 4.2. Variation of ER in function of extraction temperature, applying WAE

- Time (min) (variable), with Ratio S/L = 1/5 (constant) and Temperature = 75 °C (constant): ER values are 35.78, 35.96, and 35.45 % , for 35, 40, and 45 min, respectively (figure 4.3):

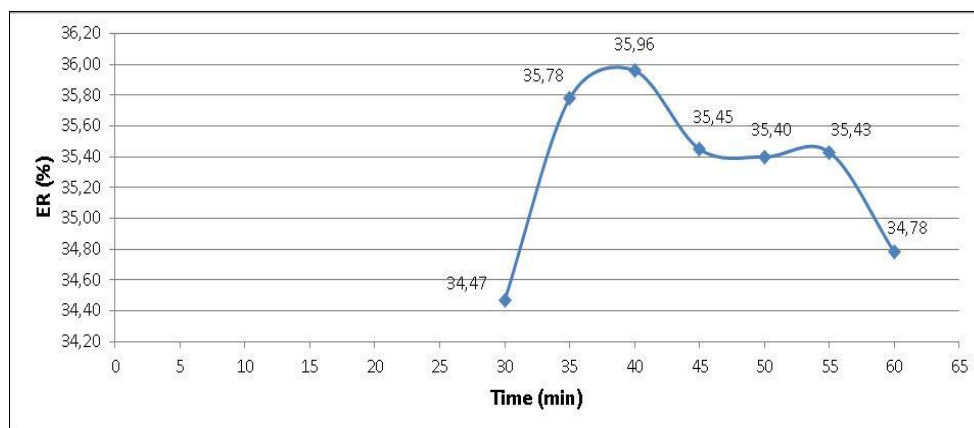


Figure 4.3. Variation of ER in function of extraction time, applying WAE

4.1.4.2. For MAE

- S/L Ratio (variable), with irradiation power = 640 W (constant) , and Time = 10 min (constant): ER values are 52.62, 67.40, and 58.60 % , for 1/6, 1/5, and 1/4 g/mL, respectively (figure 4.4):

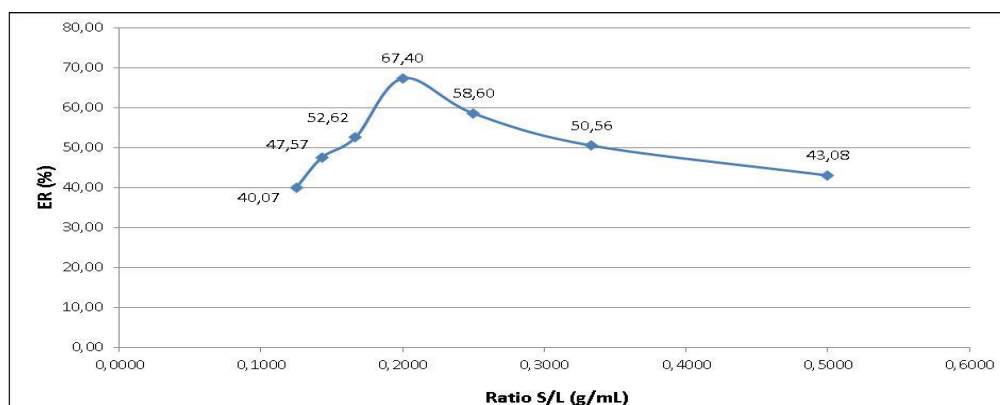


Figure 4.4. Variation of ER in function of Ratio S/L, applying MAE

- Irradiation power (W) (variable) , with Ratio S/L = 1/5 (constant) , and Time = 10 min (constant): ER values are 73.64, 76.29, and 78.88 % , for 480, 560, and 640 W, respectively (figure 4.5):

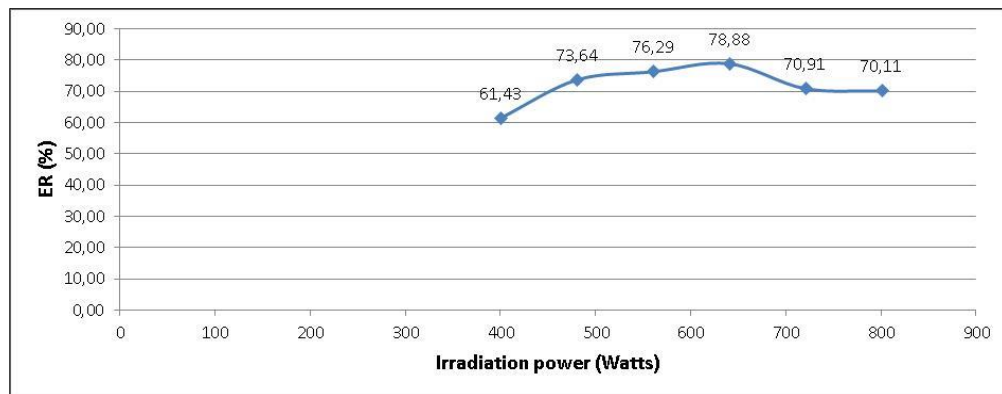


Figure 4.5. Variation of ER in function of Irradiation power, applying MAE

- Time (min) (variable), with Ratio S/L = 1/5 (constant), and irradiation power = 640 W (constant): ER values are 76.99, 75.81, and 74.78 % , for 9, 10, and 11 min, respectively (figure 4.6):

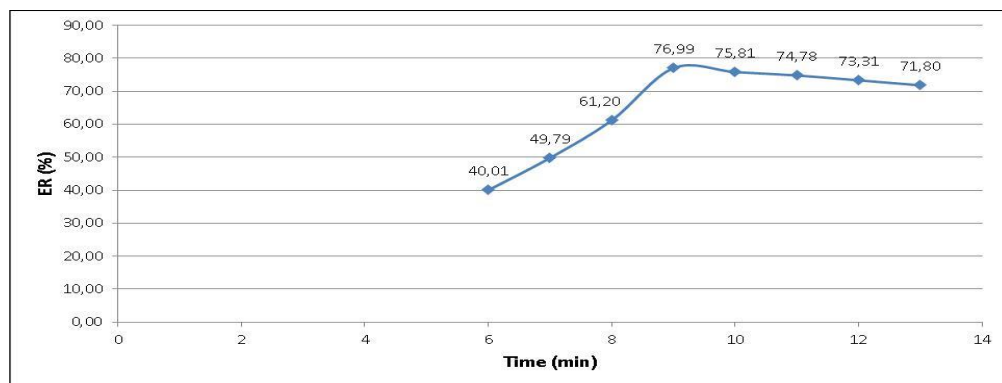


Figure 4.6. Variation of ER in function of extraction time, applying MAE

4.1.4.3. For UAE

- S/L Ratio (g/mL) (variable), with amplitude = 40 % (constant), and Time = 60 min (constant): ER values are 31.71, 30.93, and 28.99 % , for 1/5, 1/4, and 1/3 g/mL, respectively (figure 4.7):

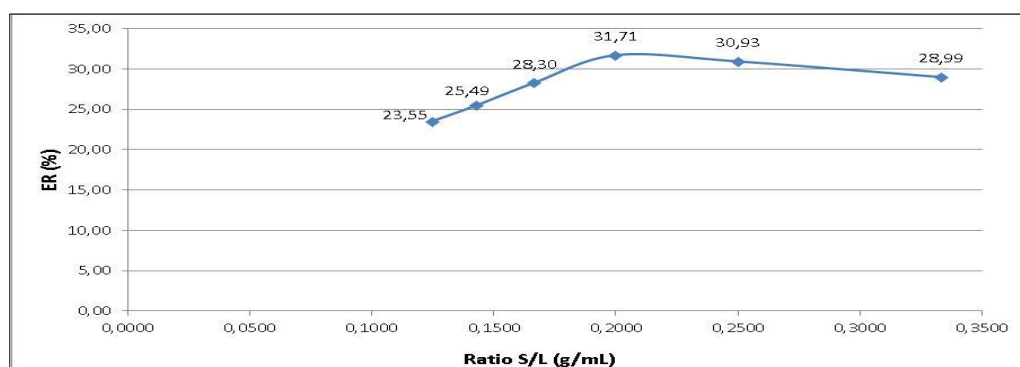


Figure 4.7. Variation of ER in function of Ratio S/L, applying UAE

- Sonication amplitude (%) (variable) , with Ratio S/L = 1/5 (constant) , and Time = 60 min (constant): ER values are 32.08, 32.41, and 32.67 % , for 30, 35, and 40 % , respectively (figure 4.8):

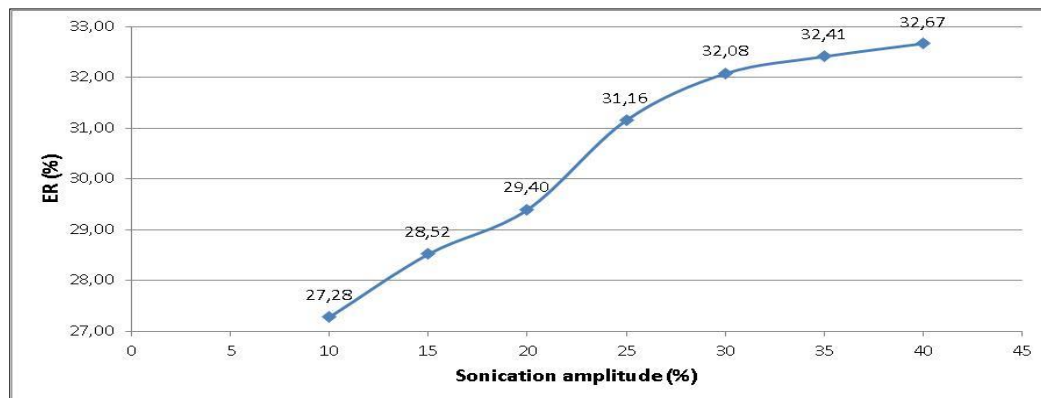


Figure 4.8. Variation of ER in function sonication amplitude, applying UAE

- Time (min) (variable), with Ratio S/L = 1/5 (constant) , and amplitude =40 % (constant): ER values are 32.71, 32.97, and 32.65 % , for 50, 55, and 60 min, respectively (figure 4.9):

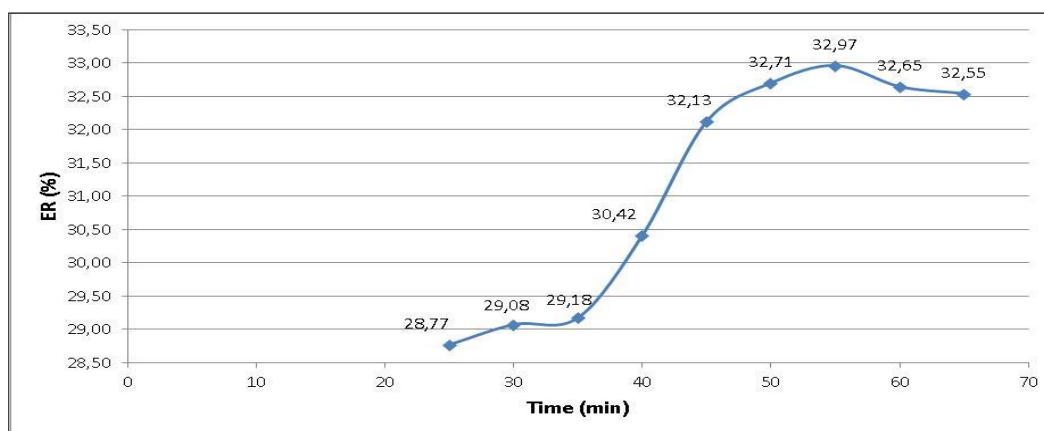


Figure 4.9. Variation of ER in function of extraction time, applying UAE

Factors and their three level (coded -1, 0, and +1) values used to optimize extraction using the three methods (WAE, MAE, and UAE), are regrouped in table 4.1.

4.1.5. Box–Behnken design (BBD)

We aimed to enhance the extraction technique via the development of a three-factor, three-level Box-Behnken Design (BBD) of response surface methodology (RSM), utilizing

three extraction methods: Water-Assisted Extraction (WAE), Microwave-Assisted Extraction (MAE), and Ultrasound-Assisted Extraction (UAE). BBD successfully optimized response (Y), indicated by extraction recovery (ER %), by the adjustment of three independent variables. We optimized the X_1 [S/L ratio (g/mL)], X_2 [energy treatment level, encompassing temperature (°C) for WAE, irradiation power (W) for MAE, and sonication amplitude (%) for UAE], and X_3 [extraction time (min)]. Through a one-factor experiment, preliminary tests determined the values of the best interval, denoted as inferior (-1), median (0), and superior (+1) levels of each of these variables, as illustrated in Table 4.1.

Table 4.1. Independent variables and their associated levels as part of the Box-Behnken plan to optimize extraction methods (WAE, MAE, UAE)

Extraction method	Factors (units)	Coded factors	Levels		
			-1	0	+1
WAE	S/L ratio (g/mL)	X_1	1/7	1/5	1/3
	Temperature (°C)	X_2	70	75	80
	Extraction time (min)	X_3	35	40	45
MAE	S/L ratio (g/mL)	X_1	1/6	1/5	1/4
	Irradiation power (W)	X_2	480	560	640
	Extraction time (min)	X_3	9	10	11
UAE	S/L ratio (g/mL)	X_1	1/5	1/4	1/3
	Sonication amplitude (%)	X_2	30	35	40
	Extraction time (min)	X_3	50	55	60

Based on the above parameters, an experimental Box-Behnken matrix was constructed, incorporating 15 trials, 12 of which corresponded to factorial points and 3 to center repetitions. The responses obtained were fitted to a quadratic polynomial model via equation (4.2).

$$Y = \beta_0 + \sum_{i=1}^k \beta_i X_i + \sum_{i=1}^k \beta_{ii} X_{ii}^2 + \sum_{ij}^k \beta_{ij} X_i X_j + \varepsilon, \quad \text{with } k = 3 \quad (4.2)$$

Y: represents the measured response - namely extraction recovery (ER) in our study. The term β_0 denotes the model constant, while β_i corresponds to the linear coefficient associated with the main effect. The term β_{ii} translates the quadratic effect of a factor, and β_{ij} designates the coefficients associated with interactions between factors. The symbols X_i and X_j represent the independent variables, and ε denotes the random error. Table 4.2 shows the results of the experimental Box-Behnken matrix, including both measured and predicted RE values.

Following the approach described by Beg and Akhter (2021), the application of quadratic response surface models proved relevant for identifying influential factors across a few

number of experiments (15 trials in this research). Optimization of the operating variables for the three extraction methods was carried out using the prediction tool “*optimizer*” integrated into Minitab software, version 17.1.0.

Table 4.2. WAE, MAE, and UAE extraction Box–Behnken Design matrix

Run	WAE					MAE					UAE				
	X ₁	X ₂	X ₃	ER (%)		X ₁	X ₂	X ₃	ER (%)		X ₁	X ₂	X ₃	ER (%)	
				Exp.	Pred.				Exp.	Pred.				Exp.	Pred.
1	1/7	70	40	35.42	35.20	1/6	480	10	62.36	62.42	1/5	30	55	32.03	31.89
2	1/3	70	40	16.39	17.11	1/4	480	10	47.16	47.18	1/3	30	55	27.24	27.27
3	1/7	80	40	33.89	33.16	1/6	640	10	42.84	42.81	1/5	40	55	32.43	32.39
4	1/3	80	40	28.41	28.62	1/4	640	10	49.58	49.51	1/3	40	55	27.78	27.91
5	1/7	75	35	33.32	34.08	1/6	560	9	61.36	61.32	1/5	35	50	31.90	32.00
6	1/3	75	35	20.10	19.92	1/4	560	9	57.50	57.50	1/3	35	50	28.15	28.08
7	1/7	75	45	31.79	31.96	1/6	560	11	67.80	67.79	1/5	35	60	32.43	32.50
8	1/3	75	45	24.26	23.49	1/4	560	11	63.06	63.09	1/3	35	60	27.43	27.32
9	1/5	70	35	28.64	28.09	1/5	480	9	63.38	63.35	1/4	30	50	30.90	30.93
10	1/5	80	35	34.35	34.31	1/5	640	9	55.61	55.66	1/4	40	50	31.41	31.34
11	1/5	70	45	30.26	30.30	1/5	480	11	70.39	70.33	1/4	30	60	30.59	30.65
12	1/5	80	45	33.03	33.57	1/5	640	11	60.71	60.74	1/4	40	60	31.40	31.36
13	1/5	75	40	33.46	33.34	1/5	560	10	44.68	44.60	1/4	35	55	30.45	30.73
14	1/5	75	40	33.55	33.34	1/5	560	10	44.71	44.60	1/4	35	55	30.71	30.73
15	1/5	75	40	33.01	33.34	1/5	560	10	44.42	44.60	1/4	35	55	31.04	30.73

4.1.6. Preparation of DPAEs

4.1.6.1. Water bath–assisted extraction (WAE)

According to several previous works (Chaira et al., 2007 ; Trigui et al., 2011; and Messadi et al., 2023), the recovery of conventional aqueous date extraction is dependent on several operating parameters, including the solid/liquid (S/L) ratio, extraction temperature and processing time. As per Nishad et al. (2019) WAE was conducted in a thermostatically controlled water-bath (model WNB 10, Memmert, Germany, 1200 W), coupled to a mechanical stirring device (type SV 2945, 230 V, 0.1 A, 50/60 Hz, 12 W, same brand), with horizontal agitation maintained at a set frequency of 150 cycles per minute (figure 4.10). Mixtures consisting of 40 g date pulp powder were combined with 280, 200 and 120 mL distilled water respectively, then subjected to thermal extraction at 70, 75 or 80°C for durations of 35, 40 or 45 minutes.



Figure 4.10. Extraction of DPAE using Water-bath Assisted Extraction (WAE) method

4.1.6.2. Microwave-assisted extraction (MAE)

As stated by Flórez et al. (2015), several factors influence the efficiency of microwave assisted extraction (MAE), including solid/liquid ratio, irradiation power, as well as treatment duration. In the protocol announced by Weremfo et al. (2020), the researchers used a household microwave oven branded MAXIMOS 23S (Maxi-power, China), functioning at a frequency set at 2450 megahertz and capable of delivering a maximum power of 800 W. The device had an internal cavity measuring 48.3 cm wide, 28.1 cm high and 38.7 cm deep, and was equipped with a condenser for water placed in the upper part to facilitate thermal control (figure 4.11). For the tests, 40 grams of date-pulp powder were dispersed in 240, 200 and 160 milliliters of distilled water, respectively, thus constituting different S/L ratios. These mixtures were then exposed to powers of 480, 560 and 640 watts for periods of 9, 10 and 11 minutes. In order to avoid any excessive rise in temperature, irradiation was applied cyclically, alternating 10 seconds of microwave emission and 5 seconds of rest. At the ending of each cycle, the temperature of the mixture was recorded using a digital electronic thermometer (model TP 300, 1.5 V) offering an accuracy of $\pm 0.1^{\circ}\text{C}$ and a measurement range from -10°C to 300°C . The final temperatures recorded for runs 1–15 were 94.5, 93.3, 98.1, 94.3, 96.9, 93.6, 97.3, 93.7, 95.6, 96.5, 96.4, 97.2, 96.2, 96.4, and 96°C , respectively.



Figure 4.11. Extraction of DPAE using Microwave Assisted Extraction (MAE) method

4.1.6.3. Ultrasound-assisted extraction (UAE)

The procedure in the UAE was conducted as detailed by López et al. (2018), with minor adjustments (figure 4.12), utilizing an ultrasonic device (Vibracell, VCX 500,115 PB, SONICS, Newtown, Connecticut, USA), which has a maximum net power output of 500 W at a frequency of 20 kHz. The vibration power output was coupled to a conventional probe, measuring 13 mm for length, 139 mm for diameter, and a maximum amplitude of 115 μm , submerged in the mixture of 40 g of date-pulp powder and 200, 160, and 120 mL of distilled-water, subjected to sonication for 50, 55, and 60 minutes, using continuous ultrasonic pulses at three sonication amplitudes (30, 35, and 40%), using the probe tip situated around 2 centimeters above the mixture. Additionally, to avoid overheating, the sonication treatment was configured to pulse mode (10 seconds ON and 10 seconds OFF); and an ice bath maintained at 40 °C ($\pm 1^\circ\text{C}$) was utilized.

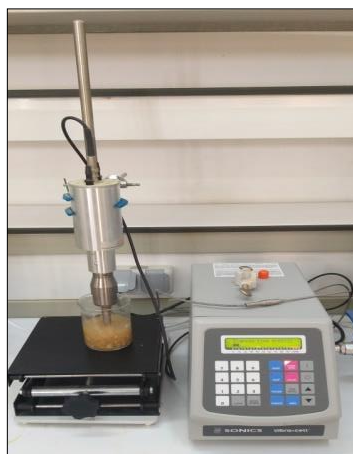


Figure 4.12. Extraction of DPAE using Ultrasound Assisted Extraction (UAE) method

The brut date extract was filtered under vacuuming utilizing Whatman filter-paper (N°4) after each experiment, and the DPAE samples were subsequently stored at 4 °C.

4.1.7. Characterization of DPAEs

4.1.7.1. Functional attributes

The physicochemical properties of the three optimized DPAE samples were examined:

- **pH** (NF V05-108, 1970) and **Titrateable acidity** (NF V05-101, 1974); were determined in accordance with the protocols described in AFNOR (1984). As the experimental protocols are identical to those described in chapter 3, only any specific modifications applied in this chapter will be presented.

- Total soluble solids (TSS): The total soluble solids (TSS) content was determined in accordance with standard (NF V 05-109, 1970), outlined in AFNOR (1984). Determination is based on measurement of the sample's brix degree using a refractometer, at a controlled temperature of $20 \pm 0.5^\circ\text{C}$. The DPAE temperature is adjusted to 20°C , and a drop is placed on the refractometer prism. The reading is taken directly and expressed in % of sucrose in fresh weight (% w/w), corresponding to the TSS of the DPAE. If the measurement is taken at a temperature other than 20°C , a correction is applied using the correction table provided for in the standard, within a range of $\pm 5^\circ\text{C}$.
- Color intensity: is determined as reported by Vickers et al. (2005), with minor adjustments, diluted DS was centrifuged at 2800 rpm for 10 min at 4°C , the supernatant diluted 10-fold with phosphate buffer (KH_2PO_4 , 25 mM and Na_2HPO_4 25 mM, pH 7.0), and filtered through a $0.45 \mu\text{m}$ PTFE filter, Absorbance was measured at 420 and 720 nm in a UV-Vis spectrophotometer (an estimate of turbidity), using a (Schimadzu, 2600 model, Japan), in duplicate. Color intensity was calculated as in equation (4.3):

$$\text{Color intensity (\%)} = \frac{1000 * (\text{Mean Abs } 420 - \text{Mean Abs } 720) * 10}{l * \text{TSS}} \quad (4.3)$$

Where:

l: Inner diameter of UV-Vis spectrophotometer cell (in cm);

TSS: soluble solids content expressed of DPAE (in °Brix).

- Non-Enzymatic Browning Index (NEBI): As described by Muñoz et al. (2012), 5 mL of the absolute ethanol was added to 5 mL of the DPAE, centrifuged for 10 min at 2800 rpm. The absorbance of the supernatant was read at 420 nm in a UV-Vis spectrophotometer (Schimadzu, 2600 model, Japan).
- Clarity: was measured in terms of the percentage of transmittance (T%) of the DPAE, at 660 nm, using a UV-Vis spectrophotometer (Schimadzu, 2600 model, Japan), as described by Mondal et al. (2013), and calculated as in equation (4.4):

$$\text{Transmittance (\%)} = 100 * 10^{-A} \quad (4.4)$$

with A: the absorbance at 660 nm.

4.1.7.2. Biochemical features

- Total sugar content: was assessed using the method of Dubois et al. (1956);
- Reducing sugar content: was measured using the method of Miller (1959)

As the experimental protocols are identical to those described in chapter 3, only any specific modifications applied in this chapter will be presented.

- Ash content (NF V 03-922): as outlined in AFNOR (1984), test DPAE sample (5g) is incinerated at $550 \pm 15^\circ\text{C}$ in an electrically heated muffle furnace, until a whitish residue of constant weight is obtained: Place the test sample of known weight in a porcelain capsule previously tared to the nearest 0.1 mg. Heat in a muffle furnace at 550°C for 5 to 6 hours, holding the temperature at 200°C for 1 hour, then return to 550°C . Allow to cool in a desiccator lined with an effective dehydrating agent (P_2O_5), then weigh several times to the nearest 0.1 mg. Continue drying to constant sample weight. The ash percentage is expressed according to the following formula (4.5):

$$\text{Ashes (\% FW)} = \frac{m_2 - m_0}{m_1 - m_0} \quad (4.5)$$

Where:

m_0 : weight of empty capsule (g);

m_1 : weight (capsule + sample) before incineration (g);

m_2 : weight (capsule + ash) after incineration (g).

- Total nitrogen matter: as described in (AFNOR (1984), the Kjeldahl method, was used, based on hot mineralization of nitrogen compounds, followed by ammonia distillation and acid-base titration. The protocol followed is as follows:

Mineralization: In a mineralization matras, 5 mL of DPAE was introduced, followed by the addition of a catalytic pellet composed of 1.5 g of potassium sulfate (K_2SO_4) and 0.15 g of copper sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), as well as 10 mL of concentrated sulfuric acid. Mineralization was carried out at 280°C for 3 hours, until a colorless solution was obtained. After cooling, a few drops of phenolphthalein and about 5 mL of distilled water were added to the solution.

Distillation: Approximately 10 mL of sodium hydroxide (NaOH 0.1 N) were gradually added to the solution, under cooling with running water, until the solution took on a violet

color, indicating the release of ammonia. The flask was then placed in a distillation unit. The released ammonia was captured in an Erlenmeyer flask containing 50 mL boric acid with an indicator mixture of methylene blue and methyl red. The solution turned green in the presence of ammonia.

Titration: The collected solution was titrated with hydrochloric acid (HCl 0.05 N) until the initial coloration (blue) returned, indicating the end of the assay.

Calculations

Total nitrogen matter content was calculated using the formula (4.6):

$$\text{TNM (\%)} = \frac{n \cdot 0.14 \cdot 100}{W} * 6.25 \quad (4.6)$$

With:

n: volume of HCl used in titration (mL);

W: dry weight of sample (g), obtained by $W = q * \text{adm}$;

Where:

q: quantity of sample taken (g);

adm: analytical dry matter content of the sample (expressed as a decimal, e.g. 95% = 0.95).

- Fat content: was determined by extraction using a Soxhlet apparatus, according to a standard gravimetric method, described by Amira et al. (2011), with minor adjustment: Approximately 20 ml of DPAE is weighted (m_0), then dried completely, and then introduced into a cellulose cartridge adapted to the extractor. Extraction was carried out with 250 mL petroleum ether (boiling point: 40-60°C) as solvent, for approximately 6 to 8 hours, until complete discoloration of the solvent at the outlet. At the end of extraction, the lipid-containing solvent was collected in a flask, and then removed by evaporation using a low-pressure rotary evaporator at 45°C. The resulting lipid residue was then dried in an oven at 105°C for 30 minutes to remove any residual traces of solvent. After cooling in a desiccator, the flask containing the extracted lipids was accurately weighed. The total lipid content was expressed as a percentage of the initial sample mass, according to the following formula (4.7):

$$\text{Lipides (\%)} = \frac{m_1 - m_0}{m_e} \quad (4.7)$$

Where:

m_1 = mass of flask after extraction and drying (g);

m_0 = mass of empty flask (g);

m_e = mass of the 20 ml of the DPAE used for extraction (g).

- Total phenolic compounds (TPC) : were determined using the Folin-Ciocalteu method, using the protocols outlined by Assadi et al. (2019) with some adjustments: 10 mL of DPAE diluted 1:10 with absolute methanol was mixed with 0.5 mL of Folin-Ciocalteu and 4 mL of sodium carbonate solution (1 M). Tubes were placed for 5 minutes in a 45°C water bath and then in a cold water bath. Absorbance was measured by a UV-vis spectrophotometer (Schimadzu, 2600 model, Japan), at 765 nm. Gallic acid was used as a calibration standard (0 to 0.07 mg/ml) (Figure 3 in annex 1). Results were expressed as mg gallic acid equivalent per ml of DPAE “mg GAE/ml of DPAE”.
- Flavonoid contents (TFC) : were determined using the protocols outlined by Assadi et al. (2019) with some adjustments, by a colorimetric method based on the formation of a flavonoid-aluminium chloride complex. A 1 mL volume of the diluted DPAE was mixed with 1 mL of 2% (w/v) methanolic aluminum chloride solution in a test tube. The mixture was incubated at room temperature for 15 minutes in the dark to allow formation of the flavonoid-aluminium complex. The absorbance of the reaction mixture was then measured at 430 nm using a UV-Visible spectrophotometer (Schimadzu, 2600 model, Japan). A calibration curve was established using standard quercetin solutions at different concentrations (0 to 0.025 mg/ml) (see Figure 4 in annex 1). Results were expressed in milligrams of quercetin equivalents per milliliter of DPAE “mg QE/ml of DPAE”.
- Pectin content: was determined as calcium pectate, using the gravimetric method described in Begum et al. (2017). This method is based on the precipitation of pectin as calcium pectate, followed by gravimetric determination. A homogeneous mixture of 50 mL of DPAE was extracted with 400 mL of HCl (0.05 N), for 2 h at 85°C, then, the volume of extract was made up to 500 mL with distilled water, then filtered through Whatman No. 4 filter paper. The filtrate was then centrifuged to remove suspended

particles. A 100 mL aliquot of the filtrate was diluted with 250 mL distilled water, and then neutralized with 1 N NaOH solution. Next, 10 mL excess NaOH (1N) was added. The mixture was left to stand at room temperature overnight. The next day, 50 mL of acetic acid (1N) was added to the mixture, followed after 5 minutes by 25 mL of calcium chloride (CaCl₂) (1N) under continuous stirring. The mixture was left to stand for 1 hour, and then boiled for 1-2 minutes to facilitate complete precipitation of calcium pectate. The solution was hot-filtered through pre-prepared filter paper (wetted with hot water, dried in an oven at 102°C for 2 hours, then weighed after cooling in a desiccator). The residue was washed extensively with near-boiling water until all chloride was removed (verified by the absence of a white precipitate with 1% silver nitrate). Finally, filter paper containing calcium pectate was dried in an oven at 100°C to constant weight, cooled in a desiccator, and then weighed with the residue.

The pectin content was calculated from the mass of calcium pectate obtained and expressed as a percentage of the mass of the initial sample, as in equation (4.8):

$$\text{Pectine (\%)} = \frac{W_{\text{pectate}} * 500 * 100}{W_{\text{sample}} * V} \quad (4.8)$$

Where:

W_{pectate} = weight of pectate de calcium (g);

W_{sample} = weight of the 50 ml of the DPAE used for extraction (g);

V: Volume of aliquot used for estimation (mL).

- Minerals: Sodium and potassium contents were determined from ashed samples using a flame absorption spectrophotometer system (Jenway, PFP7 model, England) according to (NF V76-112, 1980), AFNOR (1984), with minor adjustments. The principle of the specified method is to draw the sample into a gaseous flame of sufficient thermal energy for all the sodium and potassium present to emit its characteristic radiation, and to measure the intensity at a wavelength of 589 nm for sodium and 766.5 nm for potassium. The intensity of the absorption is proportional to the concentration of the element in the sample, according to Beer-Lambert's law. Two calibration curves (0 to 1 mg of Na /mL ; and 0 to 1 mg of Cl /mL) (presented in Figure 5 and 6 respectively, in annex 1) have been established, enabling determination of the sodium and potassium content in the DPAE analyzed.

N.B: Stock solutions were prepared by dissolving 2.542 g NaCl (for sodium) and 1.907 g KCl (for potassium) in 1 liter distilled water each, to obtain 1mg/mL solutions. Appropriate dilutions were then made to establish calibration curves.

For determination: first, mineralize the ash: Incinerate a known volume (V_0) of DPAAE, dissolve the ash obtained in 1 mL of concentrated HCl, and then carefully add 10 mL of distilled water. Heat for a few minutes in a boiling water bath until the ash is completely dissolved. Pour the solution quantitatively into a 100 ml volumetric flask, then make up to 100 ml (V_1) with distilled water. The Na and K content were calculated as mg of Na or K per 100 mL of DPAAE, as in equation (4.9):

$$\text{Sodium or Potassium (mg/100 mL DPAAE)} = \frac{X * V_1 * D}{V_0} * 100 \quad (4.9)$$

Where:

X: Concentration of Na or K, calculated from calibration curve (in mg/mL);

V_1 : Volume of the mineral solution (in mL);

D: Dilution factor (if applicable) (dimensionless);

V_0 : Volume of the DPAAE incinerated (in mL).

- Calcium and magnesium were quantified as in the study by Subedi (2023): Complexometric titration is based on the formation of stable complexes between divalent metal ions (Ca^{2+} and Mg^{2+}) and EDTA (ethylenediaminetetraacetic acid), a chelating agent. Detection of the equivalence point is ensured by a specific color indicator such as black eriochrome T (for overall $\text{Ca}^{2+} + \text{Mg}^{2+}$ determination, with wine-red to blue turn) or murexide (for specific Ca^{2+} determination at basic pH, with red to violet turn).

For total determination ($\text{Ca}^{+2} + \text{Mg}^{+2}$): Take 50 mL (V_2) of the sample in an Erlenmeyer flask, add 5 mL ammonia buffer (mixture of ammonia and ammonium chloride), to adjust pH to around 10, then add a few drops of black eriochrome T: the solution turns purple in the presence of Ca^{+2} and Mg^{+2} ions, then titrate with disodium EDTA (Na_2EDTA) 0.02 M until the color changes from violet to blue, indicating the equivalence point. Note the volume of EDTA used (V_{E1}).

For specific calcium assay (Ca alone): Take 50 mL (V_2) of sample in an Erlenmeyer flask, add 2 mL 2N NaOH (to precipitate magnesium in the form $\text{Mg}(\text{OH})_2$, during selective calcium determination), then add a small amount of murexide as an indicator (the solution

takes on a pink hue). Titrate with 0.02 M EDTA until the color changes from pink to light violet. Note the volume of EDTA used (V_{E2}). Concentrations were calculated as mg of Mg^{+2} or Ca^{+2} per 100 mL of DPAAE, as in equation (4.10, 4.11, and 4.12):

$$[Ca^{+2} + Mg^{+2}] \text{ (mg/100 ml DPAAE)} = \frac{V_{E1} * C_{EDTA} * M_{equivalent} * V_1 * D}{V_2 * V_0} * 100 \quad (4.10)$$

$$[Ca^{+2}] \text{ (mg/100 ml DPAAE)} = \frac{V_{E2} * C_{EDTA} * M_{Ca} * V_1}{V_2 * V_0} * 100 \quad (4.11)$$

$$[Mg^{+2}] \text{ (mg/100 ml DPAAE)} = [Ca^{+2} + Mg^{+2}] - [Ca^{+2}] \quad (4.12)$$

Where :

V_{E1} et V_{E2} : volume of EDTA used (m);

C_{EDTA} : molar concentration of EDTA (0.02 mol/L) ;

$M_{equivalent}$ = mean M of Ca and Mg = $(M_{Ca} + M_{Mg}) / 2 = 40.08 + 24.31 / 2 = 32.20$ g/mol;

M_{Ca} : molar mass of calcium (40.08 g/mol);

V_1 : total volume of solution (mL);

D : dilution factor (if applicable) (dimensionless) ;

V_2 : Volume of the titrated solution (in mL);

V_0 : Volume of the DPAAE incinerated (in mL).

- Sugar profile determination by GC-MS method

The experimental protocol is identical to those described in Chapter 3, with the exception of the sample to be analyzed: a dilute solution (1 μ L) of DPAAE is used for the test.

4.1.7.3. Antiradical scavenging activity

The experimental protocol followed that described in Chapter 3, with the exception of the preparation of the phenolic dry extract of DPAAE. This latter was prepared according to the method of Saleh et al. (2011), with a few minor adjustments: 90 mL absolute methanol was added to 10 mL DPAAE, and then the mixture was stirred on a magnetic plate at room temperature for 30 minutes. The resulting solution was then filtered through Whatman No. 4 filter paper and freeze-dried until completely dry.

A modified version of the procedure outlined by Braca et al. (2002) was employed to evaluate the radical-scavenging activities of the date pulp sample, prepared at various concentrations of lyophilized RPE in methanol (50-1600 μ g/ml), utilizing DPPH free radical scavenging assay. After thirty minutes, the absorbance was assessed at 517 nm and computed using the equation provided below:

$$\text{DPPH scavenging effect(\%)} = \left[\frac{(A_0 - A_t)}{A_0} \right] \times 100 \quad (4.13)$$

Where:

A₀: absorbance of the negative control (methanol) after 30 min;

A_t: absorbance of the sample after 30 min.

A linear regression analysis was performed to calculate the IC₅₀, or sample concentration (in µg/ml) necessary to lower the initial DPPH concentration by 50%. This is a measure of the samples' capacity to scavenge free radicals on DPPH.

Linear regression (LR) was conducted to determine the IC₅₀, or the methanolic extract concentration (in µg/ml) required to reduce the initial DPPH concentration by 50%. This quantifies the samples' ability to scavenge the free radicals in DPPH.

4.1.7.4. Antibacterial activity

DPAE samples were tested against five bacterial strains: *E. coli* ATCC 25922, *Bacillus cereus* ATCC 14579, *Salmonella Typhimurium* ATCC 14028, *Pseudomonas aeruginosa* ATCC 27853, and *Listeria monocytogenes* ATCC 35152. According to the method outlined in Hernández-Pérez et al. (1999) with slight modifications, the surface of each Petri plate containing Muller–Hinton agar (MH) was inoculated with a standardized suspension (0.5 McFarland) of one of the five bacterial strains using a sterile swab. Then, sterile 6 mm discs containing 50 µL of one of the tested extracts (100 mg/mL of 2.5% DMSO) were deposited on the MH surface. Discs containing gentamicin (positive control) and 2.5% DMSO (negative control) were placed with the other discs. The Petri plates were then incubated at 37 °C for 18–24 h. Each test was performed in triplicate for each bacterium and repeated three times. Antibacterial activity was estimated by measuring the inhibition halos around the discs after incubation.

4.1.8. Statistical analysis

All data were analyzed using Minitab Software (Inc., version 17.1.0). We used analysis of variance (ANOVA) followed by the Tukey's HSD (honestly significant difference) test of multiple comparisons to check if there were any statistically significant differences relative to the effect of extraction methods (WAE, MAE, and UAE) on *i*) extraction recovery (ER, %), *ii*) functional characteristics, and *iii*) biochemical features of the three DPAEs samples obtained by applying the optimum factors values. A *p*-value lower than 0.05, was used to determine the statistical significance level. The accuracy and validity of the three mathematical models were checked using the coefficient of determination R^2 (%), the adjusted coefficient of determination R^2 adj. (%), and the lack-of-fit tests.

4.2. Results and discussion

4.2.1. Fitting model

A second-order polynomial model was developed to determine optimal process conditions and the actual relationship between the response and process variables, represented by coded factors (X_1 , X_2 , and X_3) for the response Y (ER), as illustrated in equations 4.14, 4.15, and 4.16 below for WAE, MAE, and UAE, respectively. The objective was to optimize ER through multiple regressions on experimental results.

$$\begin{aligned} \text{ER exp (\%)} = & -114 - 475,8 X_1 + 1,79 X_2 + 6,26 X_3 - 496,8 X_1^2 - 0,0122 X_2^2 \\ & - 0,0586 X_3^2 + 7,113 X_1 X_2 + 2,987 X_1 X_3 - 0,0294 X_2 X_3 \end{aligned} \quad (4.14)$$

$$\begin{aligned} \text{ER exp (\%)} = & 1914,53 - 1612,6 X_1 - 0,8595 X_2 - 291,19 X_3 + 1664,6 X_1^2 \\ & + 0,000467 X_2^2 + 14,9321 X_3^2 + 1,6442 X_1 X_2 - 5,28 X_1 X_3 - 0,005969 X_2 X_3 \end{aligned} \quad (4.15)$$

$$\begin{aligned} \text{ER exp (\%)} = & 48,1 + 137,1 X_1 - 0,465 X_2 - 0,851 X_3 - 232,1 X_1^2 + 0,00468 X_2^2 \\ & + 0,00898 X_3^2 + 0,108 X_1 X_2 - 0,962 X_1 X_3 + 0,00300 X_2 X_3 \end{aligned} \quad (4.16)$$

4.2.2. Verification of the three statistical models

Table 4.3 displays the ANOVA results for fitting models of ER for the three extraction methods (WAE, MAE, and UAE). Each independent variable's significance was evaluated using *p*-values.

Table 4.3. Results of ANOVA for fitting models ER (%) for the three extraction methods (WAE, MAE, and UAE)

WAE			MAE			UAE		
Source	F-value	<i>P</i> -value	Source	F-value	<i>P</i> -value	Source	F-value	<i>P</i> -value
Model	78.03	0.0001	Model	9704.58	0.0001	Model	101.36	0.0001
Linear	161.48	0.0001	Linear	6136.50	0.0001	Linear	275.20	0.0001
X ₁	410.58	0.0001	X ₁	2593.36	0.0001	X ₁	812.43	0.0001
X ₂	72.13	0.0001	X ₂	10636.53	0.0001	X ₂	12.54	0.017
X ₃	1.72	0.247	X ₃	5179.63	0.0001	X ₃	0.64	0.460
Square	42.61	0.001	Square	20091.49	0.0001	Square	26.14	0.002
X ₁ ²	120.29	0.0001	X ₁ ²	2205.28	0.0001	X ₁ ²	69.72	0.0001
X ₂ ²	0.55	0.491	X ₂ ²	2348.48	0.0001	X ₂ ²	0.99	0.364
X ₃ ²	12.71	0.016	X ₃ ²	58685.74	0.0001	X ₃ ²	3.66	0.114
2-way Interaction	30.01	0.001	2-way Interaction	2885.74	0.0001	2-way Interaction	2.74	0.153
X ₁ X ₂	73.60	0.0001	X ₁ X ₂	8578.42	0.0001	X ₁ X ₂	0.10	0.769
X ₁ X ₃	12.98	0.016	X ₁ X ₃	13.80	0.014	X ₁ X ₃	7.67	0.039
X ₂ X ₃	3.46	0.122	X ₂ X ₃	65.01	0.0001	X ₂ X ₃	0.44	0.536
Lack-of-fit	11.75	0.079	Lack-of-fit	0.25	0.856	Lack-of-fit	0.30	0.825
R ² (%)		99.45	R ² (%)		99.99	R ² (%)		99.45
R ² adj. (%)		98.47	R ² adj. (%)		99.98	R ² adj. (%)		98.47
S (%)		0.22	S (%)		0.11	S (%)		0.22

The statistical analysis revealed promising results. The three polynomial models, as presented by equations 4, 5, and 6, show low *p*-values ($p < 0.05$) and high F-values (78.03, 9704.58, and 101.36, respectively). According to Shill et al. (2022), this shows that the models are highly significant and suitable to improve the ER using the WAE, MAE, and UAE methods. Regarding the single effect, S/L ratio and energy treatment level significantly influenced ER for all extraction methods ($p < 0.05$), whereas extraction time demonstrated a significant effect only during MAE treatment. Upon further analysis of the ANOVA results, we also identified a significant effect of the quadratic terms for S/L ratio (X_1^2) across all methods, the irradiation power (X_2^2) for MAE only, and the extraction time (X_3^2) for WAE and MAE ($p < 0.05$). Furthermore, it is worth noting that there were also some notable interaction effects ($p < 0.05$): X_1X_2 and X_1X_3 for WAE; X_1X_2 , X_1X_3 , and X_2X_3 for MAE; and X_1X_3 only for UAE (see Table 4.3).

Additionally, the R^2 coefficient values for WAE (99.45%), MAE (99.99%), and UAE (99.45%) were all close to 100% (Table 4.3), indicating that the models may be effective in accounting for the observed variance in the experimental data. Also, the adjusted R^2 coefficient values further support the potential accuracy of the model adjustments: 98.47%, 99.98%, and 98.47% for WAE, MAE, and UAE methods, respectively.

Ultimately, the insignificant lack-of-fit tests indicate that the models are suitable for the experimental data, as evidenced by their high p -values (0.079, 0.856, and 0.825, all higher than 0.05, for WAE, MAE, and UAE, respectively). The created fit models were validated using the optimized independent variables to ensure their predictability. This allowed the prediction of the optimal extraction conditions to maximize ER using BBD.

4.2.3. Extraction optimization

Figure 4.13 (a, b, c) shows the BBD optimization curves for the three techniques (WAE, MAE, UAE), as well as the (d). The optimal conditions estimated to maximize RE were: $X_1 = 1/4.68$ g/mL, $X_2 = 80^\circ\text{C}$, $X_3 = 38.63$ min for WAE; $X_1 = 1/6$ g/mL, $X_2 = 480$ W, $X_3 = 11$ min for MAE; and $X_1 = 1/5$ g/mL, $X_2 = 40\%$, $X_3 = 60$ min for UAE. Figure 4.13(d) shows the maximum experimental ER values obtained: $34.66 \pm 1.11\%$, $79.90 \pm 1.54\%$, and $31.43 \pm 1.21\%$.

Differences in ER between methods are significant ($p < 0.05$). Experimental values closely matched predictions ($R^2 = 99.8\%$): 35.79% ($d = 0.93$) for WAE, 81.06% ($d = 1$) for MAE, and 32.94% ($d = 1$) for UAE.

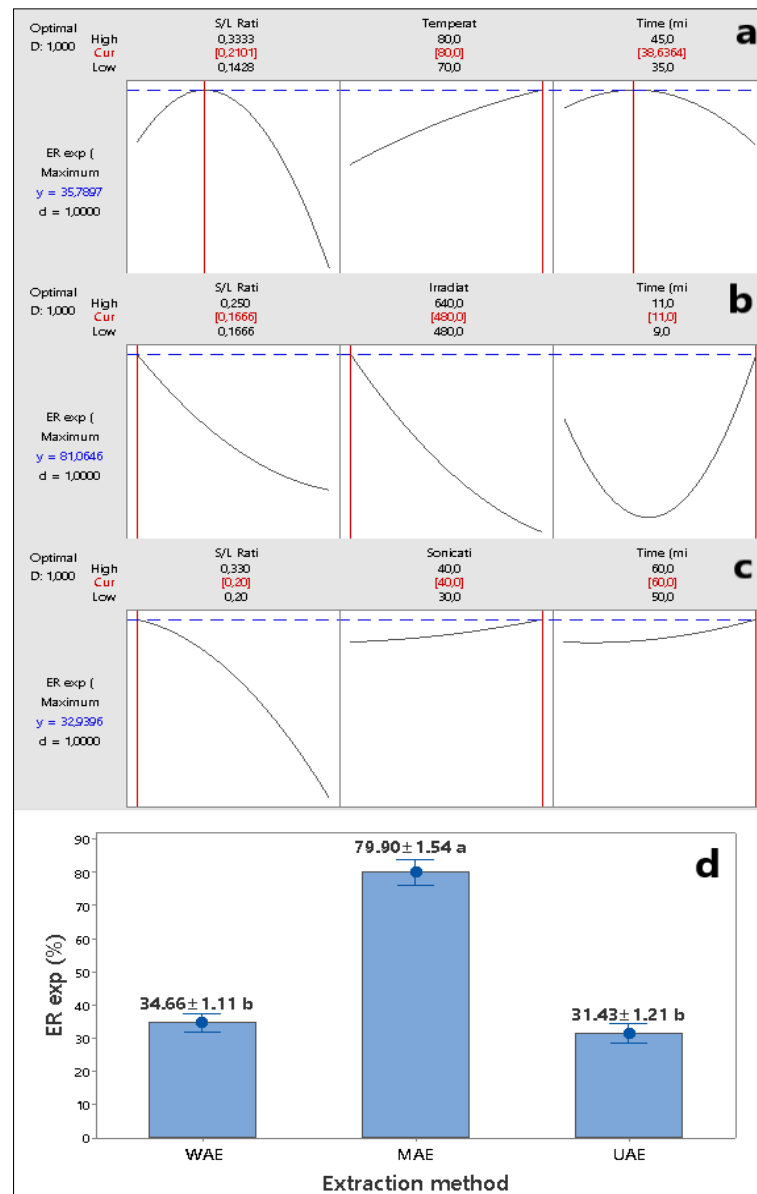


Figure 4.13. Optimization plot values of ER (%) derived from date pulp extracted by (a) WAE, (b) MAE, and (c) UAE, and (d) their mean experimental ER (%) values obtained by applying the optimum conditions predicted.

4.2.4. Effect of extraction parameters on recovery

The analysis of the results presented in Figure 4.14 highlights the variability of ER as a function of the extraction method employed and the configuration of experimental parameters. This predictive modeling enables dynamic analysis: the translation of the vertical red line along the x-axis corresponds to the level's adjustment of the parameter studied, resulting in automatic reconfiguration of the diagrams and instant recalculation of predicted responses on the blue y-axis and desirability values. In the rest of the analysis, we will examine the single effect of each parameter on the ER, keeping the two other extraction variables at their optimal

level predicted. The effect of extraction parameters on recovery is presented in factorial plots for WAE, MAE, and UAE methods, in figure 4.14 a,b, and c respectively.

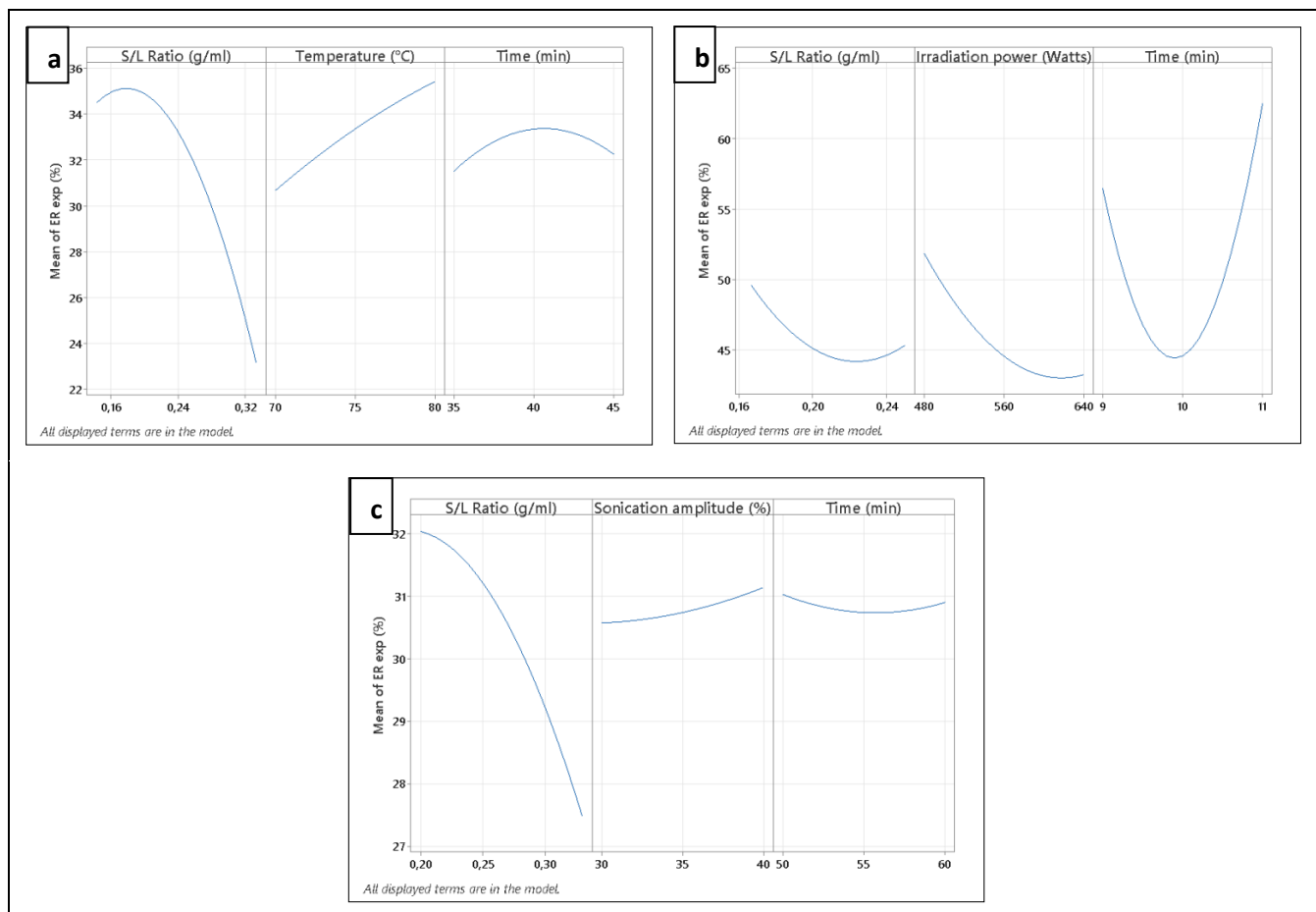


Figure 4.14. Factorial plot of ER exp (%) vs independent factors (a) WAE, (b) MAE, and (c) UAE

4.2.4.1. Solid/liquid ratio

As shown in figure 4.14a, the impact of the S/L ratio on the efficiency of the WAE method was significant. ER increased parabolically from 33.55% to 35.79% when the S/L ratio increased from 1/7 to 1/4.68 g/mL, while the other extraction parameters remained constant (80 °C and 38.63 min). A solvent volume of less than 280 mL for 40 g of date pulp powder may increase the powder analyte transfer in the extraction medium and generate more pulp aqueous-soluble solids.

As affirmed by Mgoma et al. (2021), this observation may be explained by Fick's law: the flow rate of a compound is directly proportional to the concentration gradient. However, when S/L ratio increased to 1/3 g/mL, ER decreased progressively from 35.79% to 28.23%, suggesting that insufficient solvents may also affect component extraction recoveries

(incomplete extraction). In the same manner, using microwaving, increasing this ratio over 1/6 g/mL to 1/4 g/mL led to an increase in the viscosity of the date pulp-water powder mixture, which in turn reduced diffusion rate and significantly decreased ER from 81.06% to 65.39% (figure 4.5b). This phenomenon elucidates the negative correlation observed between the S/L ratio and ER, corroborating the results reported by El-Sharnouby et al. (2014). The same was true for the UAE method: a low S/L ratio favored better ultrasound transmission, releasing more compounds and increasing ER. At a higher solid/liquid ratio (1/3 g/mL), there was rapid solvent saturation and limited solubilization of extracted compounds, resulting in a decrease in ER from 32.94% to 27.83% (figure 4.14c). Furthermore, the significant quadratic term (X_1^2) for all methods supports our arguments (Table 3), indicating that the impact of the S/L ratio on ER follows a parabolic curve (Figure 4.13 a, b, and c).

4.2.4.2. Energy treatment level

Using the water bath method, ER increased slightly from 32.35% to 35.78% with increasing temperature from 70 to 80 °C, as shown in figure 4.5a. Probably, increasing temperatures cause structure disruption and increase diffusion, which could make soluble chemicals in date pulp powder easier to extract, increasing the ER. Our suggestions are supported by Kadlezir et al. (2024) when applying the water bath method, temperature significantly affects vitamin C, total polyphenol, and free amino acid contents of the aqueous date pulp extract. Those three responses increased with increasing temperature, from 73.5 mg/L, 3.61 g GA/100 g, and 497.2 mg/L at 25 °C, to values of 88.26 mg/L, 4.78 g GA/100 g, and 565.42 mg/L at 95 °C, respectively. Perhaps those constituents present in our samples, also increase, increasing ER. In contrast, this then decreased progressively from 81.06% to 60.5% when irradiation was increased from 480 to 640 W (figure 4.5b). This can be explained by microwaves rapidly heating water due to its dielectric characteristics (high constant and dissipation factor) (Mandal et al., 2017). Water absorbs microwaves powerfully at high power, causing an internal pressure that damages plant cells and promotes evaporation, disturbing the ideal solvent-to-solid ratio and limiting solute mobility (Flórez et al., 2015 and Chambaud 2023).

Furthermore, the decrease in ER can be explained by the observations of Rocha et al. (2021), which indicate that excessive overheating leads to thermal degradation of sugars and other sensitive compounds, reducing their recovery in the final extract. With regard to UAE, ER increased slightly from 32.29% to 32.94% with an increase in amplitude from 30% to 40% (figure 4.5c). This result is in line with Entezari et al. (2004), who extracted juice from date pulp and observed that a higher intensity resulted in a higher extraction rate compared to a lower one.

4.2.4.3. Extraction time

As shown in figure 4.14a, time was revealed to be not significant for WAE ($p > 0.05$). Under operating conditions set at a solid/liquid ratio of 1/4.68 g/mL and a temperature of 80°C, ER showed a slight increase from 34.95% to 35.78% over the time interval from 35 to 38.63 minutes. This slight improvement is due to a little continuous interaction between the matrix and the water. However, the extension of the extraction time (from 38.63 to 45 min) also resulted in a degradation of certain water-soluble compounds, as approved by Hasni et al. (2021).

During sonication treatment, time was revealed to be not significant ($p > 0.05$). A boost in extraction time from 50 to 60 min led to a minor increase in RE from 32.29% to 32.94% (figure 4.14c). It is likely that, at around 50 min, the extraction process reaches its maximum efficiency, and that the extended time is mainly used to extract compounds that are more difficult to dissolve.

The conventional extraction method achieved a maximum recovery of 35.78% in just 38.63 min at a temperature of 80 °C, approximately twice as fast as UAE. Indeed, with a sonication intensity of 40%, sonication produced a comparable recovery of 32.94% but in 60 minutes, despite a S/L ratio held constant at approximately 1/5. This result contradicts the observations of Vinatoru et al. (2017), who, in their literature review, discussed advances in extraction methods for plant compounds and highlighted the advantages of UAE in significantly reducing the time required to reach extraction equilibrium. It is likely that the level of ultrasonic power applied in this study (40%) was insufficient to induce rapid optimal cavitation, thus limiting the acceleration of extraction by sonication.

MAE shows a significant influence of time on ER ($p < 0.05$). Figure 4.13b reveals a parabolic curve-shaped relationship between time and ER ($p < 0.05$ for quadratic term X_3^2), indicating that either too little or too much extraction time is not optimal. Insufficient time limits compound extraction, while excessive time (over 11 min) may lead to degradation or limit release. Duration of approximately 11 min seems ideal for maximizing ER (figure 4.14b). Thus, the best extraction time must optimize ER while preserving nutritional content.

Finally, the data presented in Table 4.3 highlight the multifactorial nature of the extraction mechanism and the complexity of 2-way interactions (already mentioned above) between operating parameters. As highlighted by Sridhar et al. (2022), these interactions, specific to each extraction technique, significantly influence compound flow in the mixture. For the conventional method, temperature and time, combined with an appropriate S/L ratio, dynamically modulate analyte solubility and diffusion. In the case of MAE, irradiation power must be fine-tuned according to the S/L ratio and exposure time, finely determining heat transfer and extraction selectivity to avoid thermal degradation while maximizing extraction efficiency. Finally, for UAE, maximum cavitation depends on choosing the right S/L ratio combined with optimal extraction time, irrespective of amplitude level. These results confirm the multifactorial nature of extraction processes and underline the importance of rigorous optimization of operating conditions for each method.

As cited above, the maximum ER value of the water bath and ultrasonic methods is significantly lower than that of microwave extraction. This result can be explained by the limitations of convective heat transfer in conventional heating and the formation of a layer of material around the pulp powder during sonication, which hinders the diffusion of constituents. Microwaves, on the other hand, disrupt this protective layer around the pulp powder and interact directly with the new water molecules present, thereby increasing extraction recovery. These observations corroborate the work of Flórez et al. (2015) and Vinatoru et al. (2017), who showed that a rapid increase in temperature due to microwaves promotes more efficient extraction. Even when the extraction parameters were set at minimum levels for extraction recovery (1/4 g/mL, 640 W, and 10 minutes), ER obtained with the microwave method still amounted to 49.58% (trial 4 in Table 4.2), significantly higher than those of the conventional and ultrasonic methods. It is worth noting that microwave

heating could be considered in the beverage sector as an alternative to conventional techniques (Cendres et al., 2012 and Turk et al., 2017).

4.2.5. *Effect of extraction methods on the quality of DPAE*

Tables 4.4 and 4.5 summarize the functional characteristics and biochemical features of the DPAEs (figure 4.15) obtained by applying the optimum experimental conditions for each extraction method (WAE, MAE, and UAE). The observable characteristics of DPAE were significantly impacted by the extraction technique employed, as follows:

4.2.5.1. pH and titratable acidity

Statistical analysis reveals significant variations ($p < 0.05$) in pH and titratable acidity values between extraction methods. DPAEs show a mean pH ranging from 5.44 ± 0.01 to 5.78 ± 0.05 and titratable acidity from 0.19 to 0.34 ± 0.016 g of citric acid equivalent/100 mL, in agreement with the values reported by Ganbi et al. (2012) However, our titratable acidity levels are significantly higher than those of Ogblechi et al. (2014) (0.048 g of citric acid equivalent/100 mL), whose extraction process was based on a pulverizer and screw press. Although high-temperature sterilization is integrated, Ogblechi's mechanical extraction, without intensification techniques (microwaves or ultrasound), limits acid extraction, while prolonged sterilization can degrade certain sensitive acids. This optimization of modern methods thus favors extracts that are more stable and better suited to functional applications.

4.2.5.2. Total ash and minerals

Analysis of total ash and minerals revealed significant variations between extraction methods ($p < 0.05$), particularly for K, Ca, and Mg concentrations, while Na content remained stable. These differences suggest variable extraction efficiencies for different minerals, reflecting variable extraction efficiencies depending on the elements considered. Meanwhile, Samsalee and Sothornvit (2022) evaluated the mineral extraction from used coffee grounds and demonstrated that methods such as autoclaving and ultrasonic favor increased concentrations of phosphorus, potassium, calcium, and magnesium, indicating that these easily soluble elements are preferentially extracted under intensification conditions.

Table 4.4. The most important functional characteristics of the three optimized DPAE

Characteristics \ Extraction method	WAE	MAE	UAE
pH	5.54 ± 0.08 ^b	5.44 ± 0.02 ^b	5.78 ± 0.05 ^a
Total soluble solids (TSS) (% FW)	14.06 ± 0.11 ^a	14.33 ± 0.11 ^a	11.73 ± 0.3 ^b
Clarity (T ₆₆₀ %)	47.46 ± 5.58 ^b	28.58 ± 5.65 ^c	64.55 ± 5.65 ^a
Color intensity (index × 10 ⁻³)	73.45 ± 0.54 ^b	76.85 ± 0.46 ^a	68.82 ± 0.48 ^c
Non-enzymatic browning index (NEBI)	0.35 ± 0.01 ^b	0.46 ± 0.07 ^a	0.27 ^b

Data shown are mean ± SD (n = 3); superscripts a, b, and c indicate significant differences according to Tukey's test. Values with different superscripts within the same line are significantly different at p < 0.05.

Table 4.5. Biochemical features of the three optimized DPAE samples

Characteristics \ Extraction method	WAE	MAE	UAE
Total ash (% FW)	0.23 ± 0.01 ^{a,b}	0.28 ± 0.03 ^a	0.17 ± 0.03 ^b
Titrate acidity ¹	0.27 ± 0.01 ^b	0.34 ± 0.01 ^a	0.19 ^c
Total phenolic content (TPC) ²	1.42 ± 0.03 ^b	1.69 ± 0.04 ^a	1.01 ^c
Total flavonoid content (TFC) ³	0.16 ^b	0.18 ^a	0.15 ^b
Total sugar ⁴	19.76 ± 0.11 ^b	22.23 ± 0.23 ^a	18.2 ± 0.43 ^c
Reducing sugar ⁴	5.03 ± 0.95 ^c	9.03 ± 0.05 ^b	11.73 ± 0.55 ^a
Sucrose ⁵	139.12 ± 7.71 ^a	117.34 ± 5.27 ^b	56.01 ± 0.84 ^c
Glucose ⁵	20.35 ± 0.83 ^c	32.86 ± 0.35 ^b	50.86 ± 3.68 ^a
Fructose ⁵	22.08 ± 0.99 ^c	35.04 ± 1.41 ^b	53.57 ± 4.16 ^a
Protein (total nitrogen matter) ⁴	0.23 ± 0.01 ^{a,b}	0.24 ^a	0.20 ± 0.01 ^b
Fat ⁴	0.13 ± 0.05 ^a	0.18 ± 0.09 ^a	0.16 ± 0.05 ^a
Pectin amount ⁶	0.26 ^b	0.4 ± 0.01 ^a	0.2 ± 0.01 ^c
Potassium ⁷	112.18 ± 6.8 ^a	105.23 ± 12.88 ^a	76.87 ± 6.67 ^b
Sodium ⁷	33.49 ± 4.13 ^a	31.68 ± 2.7 ^a	36.19 ± 3.12 ^a
Calcium ⁷	53.85 ± 3.34 ^a	49.10 ± 5.98 ^b	23.33 ± 5.77 ^a
Magnesium ⁷	55.33 ± 5.03 ^a	51.33 ± 4.16 ^a	23.33 ± 5.77 ^b

Data shown are mean ± SD (n = 3); superscripts a, b, and c indicate significant differences according to Tukey's test. Values with different superscripts within the same line are significantly different at p < 0.05.

¹ expressed as g of citric acid eq. /100 mL of DPAE; ² expressed as mg GAE/mL of DPAE;

³ expressed as mg QE/mL of DPAE; ⁴ expressed as g/100 mL of DPAE; ⁵ expressed as mg/mL of DPAE;

⁶ expressed as % calcium pectate of FW; ⁷ expressed as mg/100 mL of DPAE

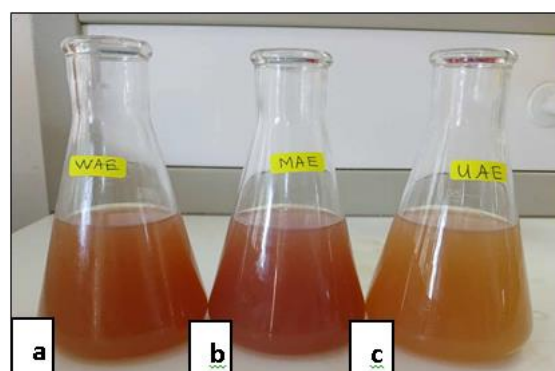


Figure 4.15. Date palm aqueous extracts obtained by applying the optimum conditions predicted, applying (a) WAE, (b) MAE, and (c) UAE

4.2.5.3. Pectin amount and clarity

DPAE obtained by MAE showed higher pectin recovery compared to WAE and UAE (Table 4). The heat generated quickly by microwave irradiation can enhance the release of polysaccharide compounds such as pectin, even though no previous studies have specifically explored microwaving for dates. The high pectin content of the DPAE could contribute to its potential retention and stabilization properties, as pectin is known for its ability to form gels in the presence of acids and sugars. In this respect, Masmoudi et al. (2010) demonstrated in a low-sugar (45%) date jelly formulation that the interaction between lemon pectin and *Deglet Nour* date pulp promoted gelling by thermo-controlled methylation, suggesting a synergistic stabilization mechanism via sucrose-calcium gel interactions.

Clarity is an essential attribute for ready-to-serve beverages based on date fruit. Thus, the removal of suspended particles such as pectin is crucial, as stated by Kulkarni et al. (2010). Thus, a higher transmittance indicates a clearer extract (Hou et al., 2023). In this study, DPAE obtained by sonication had the highest clarity ($64.55\% \pm 5.65\%$) at the lowest pectin content ($0.2\% \pm 0.01\%$ FW) (Table 4.4, 4.5, and figure 4.15). These results suggest that sonication promotes juice clarification by reducing pectin content, making it a promising and effective method for improving the clarity of fruit juices. Our results are in accordance with those of Santhirasegaram et al. (2013), where juices sonicated for 15 and 30 minutes showed a clear improvement in clarity.

4.2.5.4. Non-enzymatic browning index and color intensity

NEBI and color intensity of our DPAEs were found to be significantly affected by the three extraction methods ($p < 0.05$); MAE's extract had the highest NEBI, with an improvement in color intensity, followed by conventional and ultrasonic methods (Table 4.4). These results suggest that ultrasonic methods target specific compounds with distinct solubility, making aqueous date palm pulp extract suitable for the production of light-colored energy drinks (Fikry et al., 2023).

Previous studies of Patrignani et al. (2021) and El-Nagga and Abd El-Tawab (2012) have linked microwave quick heating to accelerated non-enzymatic processes and brown pigment formation. This accumulation then contributes to the increase in color intensity. In this context, Yilmaz and Toledo (2005) Yilmaz and Toledo (2005) agreed that heat-induced non-enzymatic

browning as Maillard reaction leads to the chemical transformation of macronutrients, resulting in the generation and accumulation of compounds with strong antioxidant capacity (in this study, IC_{50} was determined at $729.80 \pm 12.87 \mu\text{g/mL}$ for the methanolic extract of DPAAE extracted by MAE).

4.2.5.5. Phenolic compounds and antioxidant activity

Our results show that MAE achieved significantly higher contents of total phenolic compounds and flavonoids under optimal conditions ($p < 0.05$), with $1.69 \pm 0.04 \text{ mg GAE/mL}$ for TPC and 0.18 mg QE/mL for TFC, highlighting the increased efficiency of MAE in extracting these bioactive compounds.

Microwave-assisted extraction enables the rapid and efficient isolation of polyphenols with minimal use of solvents. Solvents that effectively absorb microwaves, such as water, are particularly recommended for their efficient heat transfer and preservation of thermolabile compounds (Yussof et al., 2022).

MAE influences both the yield and the integrity of bioactive compounds. By accelerating the process, microwave-assisted extraction minimizes the degradation of sensitive molecules. However, if not properly optimized, it may lead to the formation of undesirable by-products or partial degradation of some compounds [60]. The phenolic structure of these compounds gives them enhanced antioxidant properties, including scavenging DPPH radical's capacity. Our optimized DPAAE presented an IC_{50} of $729.80 \pm 12.87 \mu\text{g/mL}$ of methanolic extract (Figure 4.16), whereas, according to Nariya et al. (2013), the IC_{50} of ascorbic acid is $6.1 \mu\text{g/mL}$. This indicates that ascorbic acid is approximately 120 times more effective at neutralizing free radicals, meaning that a significantly higher concentration of our DPAAE is required to achieve a comparable antioxidant effect. These results confirm that microwave irradiation is the most effective method for extracting natural bioactive compounds from date pulp. Djaoud et al. (2020) support our recommendation. Besides these properties, the natural date pulp extract obtained by microwave irradiation could constitute an ideal functional by-product as an adjuvant in food formulations, contributing effectively to the extension of product shelf-life (Menai et al., 2024).

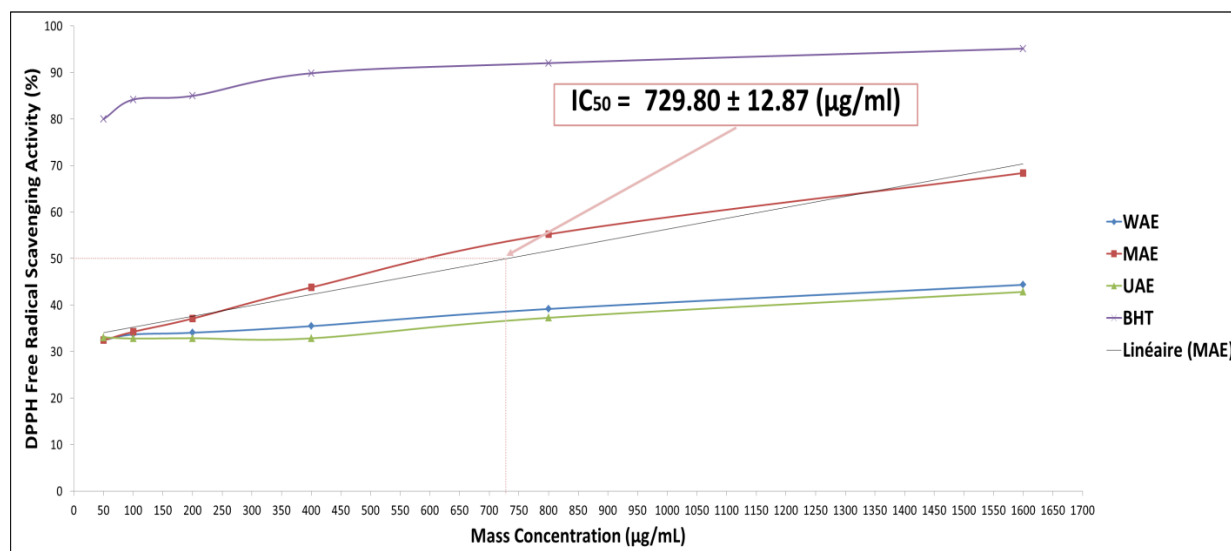


Figure 4.16. The antiradical scavenging activity curves of the three optimized DPAE

4.2.5.6. Total soluble solids and sugar content

The TSS in our extracts varied substantially ($p < 0.05$), with MAE extract exhibiting the highest amount ($14.33\% \pm 0.11\%$ FW). Date pulp mostly consists of simple sugars and disaccharides, mainly glucose, fructose, and sucrose, which are readily absorbed by the body, accompanied by low levels of cellulose and starch (Ashraf & Hamidi-Esfahani, 2011). Figure 4.17 shows the sugar chromatograms for the three extract samples obtained under the optimum conditions for each extraction method, using the GC-MS method.

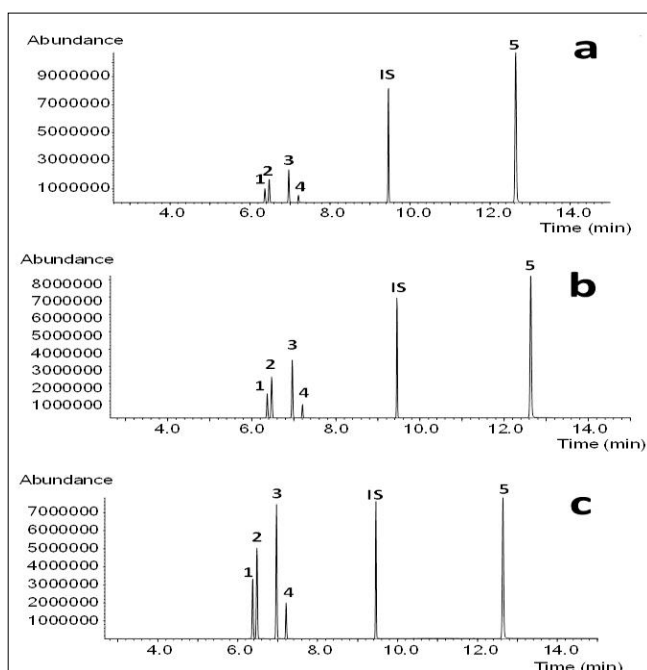


Figure 4.17: GC-MS chromatograms of the three DPAE obtained by applying the optimum values of the three extraction methods:

(a) WAE, (b) MAE, and (c) UAE.

- 1: D-Fructose, 1,3,4,5, 6-pentakis-O-(trimethylsilyl)-,O-methyloxime(1); RT = 6.36 min.
 - 2: D-Fructose, 1,3,4,5,6-pentakis-O-(trimethylsilyl)-,O-methyloxime(2); RT = 6.47 min.
 - 3: D-Glucose, 2,3,4,5,6-pentakis-O- (trimethylsilyl)-,O- methyloxime (syn); RT = 6.96 min.
 - 4: D-Glucose, 2,3,4,5,6-pentakis-O-(trimethylsilyl)-,O-methyloxime (anti); RT = 7.20 min.
 - 5: Sucrose, α -D-Glucopyranosid,1,3,4,6-tetrakis-O-(trimethylsilyl)— β -D fructofuranosyl—2,3, 4,6- tetrakis-O-(trimethylsilyl); RT = 12.63 min.
- IS: Internal standard: phenyl- β -glucopyranoside; RT = 9.45 min.

The five methylated sugar compounds, corresponding to peaks numbered 1–5, include the pyranose and furanose forms of fructose (*syn* and *anti* isomers numbered 1 and 2), the *E* and *Z* isomers of glucose, and sucrose. In addition, a blank pyridine sample was used as an internal standard. The RT in GC-MS analysis is influenced by sample treatment, injection conditions, and the type of compound analyzed (Whitney et al., 2007), as well as by the stereo-chemical configuration of sugars (α and β isomers for monosaccharides and disaccharides) (Kranenburg et al., 2019).

According to the data in Table 4, carbohydrates differed significantly ($p < 0.05$) between extraction methods, with the microwave method yielding the highest sugar extract (22.23 ± 0.23 g/100 mL of DPAAE). More specifically, taking into account the inherent properties of the extracted carbohydrates, it was found that the amounts of reducing sugars (glucose and fructose) varied significantly between methods, with the UAE method offering the highest extraction yield (Figure 4.17). With regard to conventional methods, Messadi et al. (2023) attempted to optimize the extraction of sugars from the Tunisian cultivar *Kentichi*, obtaining a total sugar content of 16.01 ± 0.03 g/100 mL aqueous extract, lower than our WAE sample (19.76 ± 0.11 g/100 mL).

As per Trigui et al. (2011), This difference can be attributed to sugar diffusivity coefficients of the pulp matrix, which vary according to the date pulp texture between the two cultivars. In this context, Gabsi et al. (2013) developed a CFD (computational fluid dynamics) model to predict and compare the yield of natural sugar compounds extracted from three Tunisian cultivars: *Menakher*, *Lemsi*, and *Alligue*. The model takes into account the sugar diffusivity as a function of internal fruit matrix parameters, date/water ratio, and other process-specific characteristics. They found that optimal diffusion conditions were achieved at 50 rpm and 0.75, for stirring speed and date/water ratio, respectively, using the *Lemsi* date cultivar. This theoretical framework also explains the apparent differences between our results and those of Chaira et al. (2007) who applied the conventional extraction method and found that the mean values of glucose and fructose amounts of the three date extracts from *Deglet Nour's* cultivar were 2.31 ± 0.34 g/100 mL and 3.41 ± 0.68 g/100 mL, respectively, slightly higher than our samples (20.35 ± 0.83 and 22.08 ± 0.99 mg/mL of DPAAE, respectively). These results could be explained by the fact that initial glucose and fructose amounts of the pulp of *Deglet Nour*

cultivars with a semi-soft consistency were higher than those of *Mech Degla*, a dry one. Our proposals were based on the classification of 93 cultivars of Algerian date palm fruits into several consistency classes based on their sucrose and reducing sugar content established by Belguedj et al. (2002).

4.2.5.7. Protein and fat contents

All extracts contained traces of proteins and lipids, with the highest being that extracted by MAE (0.24 and 0.18 ± 0.09 g/100 mL of DPAAE, respectively), followed by the water bath method (0.23 ± 0.01 and 0.13 ± 0.05 g/100 mL of DPAAE, respectively). In their study, Masmoudi et al. (2008), found that date juice obtained using the conventional method (hot plate with continuous stirring) resulted in low protein content (1.79 ± 0.10 g/100 DM).

4.2.5.8. Antibacterial activity

Figure 4.18 and Table 4.6 display the findings of the antibacterial activity of the three optimized DPAAE. The variable bacterial inhibition seems to be the result of the action of the different compounds present in the three DPAAEs. On the other hand, it has been shown that the extracts studied do not show antibacterial activity, except for the one observed against *E. coli*, due to the inappropriateness of the diffusion method for poorly water-soluble agents. This proposal is supported by the results obtained by Hassim et al. (2015).

In fact, only aqueous date extract obtained by the water bath method containing 1.42 mg GAE/mL polyphenols showed significant antibacterial activity against *E. coli* ($p < 0.05$) with an inhibition diameter of 18 ± 2 mm. However, the antibacterial activity of date extracts cannot be attributed only to their total polyphenol content but also to the presence of specific phenolic compounds, as demonstrated by several studies, including that of El Sohaimy et al. (2015), which identified, by HPLC, several phenolic compounds present in aqueous date extracts obtained by the conventional method (date and distilled water stirred for 60 min at 25 °C) with antibacterial properties, namely phenolic acids (gallic acid: 7.51 ± 0.123 µg/g, itaconic acid: 6.40 ± 0.113 µg/g, and ferulic acid: 0.15 ± 0.194 µg/g), coumarins (esculetin: 15.11 ± 0.213 µg/g), and tannins (tannic acid: 2.85 ± 0.097 µg/g).

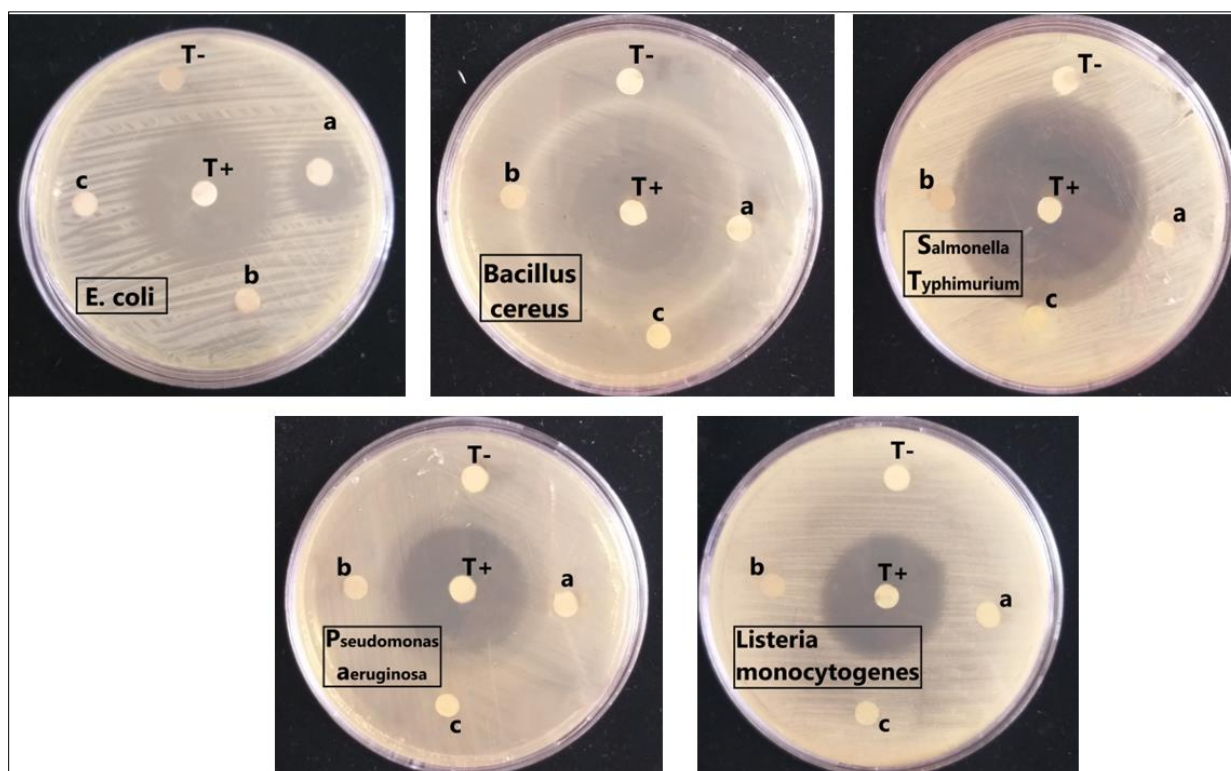


Figure 4.18. Antibacterial activity of the three optimized DPAE obtained using (a) WAE, (b) MAE, and (c) UAE. T- and T+ designate the positive (gentamicin) and the negative (2.5% DMSO) controls, respectively.

Table 4.6. Antibacterial activity of the three DPAE obtained using WAE, MAE, and UAE (diameter of inhibition zone per mm)

Extraction method	Strains				
	<i>E. coli</i> ATCC 25922	<i>B. cereus</i> ATCC 14579	<i>S.</i> <i>Typhimurium</i> ATCC 14028	<i>P. aeruginosa</i> ATCC 27853	<i>L.</i> <i>Monocytogenes</i> ATCC 35152
T ⁺	42.33 ± 2.52 ^a	41.67 ± 2.08 ^a	55.67 ± 4.04 ^a	34.66 ± 1.52 ^a	32 ± 1 ^a
WAE	18 ± 2 ^b	6 ^b	6 ^b	6 ^b	6 ^b
MAE	6 ^c	6 ^b	6 ^b	6 ^b	6 ^b
UAE	6 ^c	6 ^b	6 ^b	6 ^b	6 ^b
T ⁻	6 ^c	6 ^b	6 ^b	6 ^b	6 ^b

Data shown are mean ± SD (n = 3); superscripts a, b, and c indicate significant differences according to Tukey's test. Values with different superscripts within the same column are significantly different at p < 0.05.

However, no antibacterial effect was recorded for this extract against the other bacteria and for the two other extracts against all the bacteria tested (p > 0.05). In Saleh and Otaibi's study (2013), no antibacterial effect against *E. coli* was detected for any of the aqueous date pulp extracts of the three Saudi cultivars studied (*Khulase*, *Sheshi*, and *Rezaza*). On the other hand, our results are in concordance with a previous study by Al-daihan and Shafi Bhat (2012), in which date aqueous extracts from *Mosaiifah* Saudi cultivar were proven to have anti-*E. coli* effect, with an inhibition zone of 11 ± 0.88 mm. Although this was effective, its effect was lower than that of our WAE extract. Also, this extract produced a zone of inhibition of

11 ± 0.57 mm against *P. aeruginosa*, indicating a higher antibacterial efficacy than our extracts (6 mm). This shows that DPAAE is less effective than some other alternative extraction methods, and that extraction conditions and date cultivars greatly affect antibacterial effectiveness, as confirmed by Bhaskaracharya et al. (2023). Furthermore, we can conclude that more intensive methods (such as those using water or thermal processes) seem to favor a better release of active antibacterial compounds. It is noteworthy that *Escherichia coli* is a Gram-negative bacterium recognized as one of the most common bacterial species encountered in nosocomial infections in humans, including urinary and enteric infections. This bacterium is also known for the development of bio resistance against some antibiotics (Pitout, 2012). The effectiveness of the DPAAE obtained by the water bath method seems promising because it may constitute a natural alternative to antibiotics. Additionally, this efficiency suggests the presence of some specific anti-*E. coli* bioactive compounds like polyphenols (1.42 ± 0.03 mg GAE/mL of DPAAE).

The MAE and UAE treatments offer rapid and efficient ways to extract bioactive compounds. However, the lack of antibacterial activity could be explained by the fact that the inhibitory effect of the targeted bioactive compound depends on its concentration in our UAE/MAE extract by bacterial outer membrane resistance, as reported by Gowda et al. (2022). i.e., under the optimal extraction conditions applied in the present study, they may inadvertently lead to the degradation of these compounds. In this context, as reported by Chan et al. (2011), high microwave power raises the temperature of the solvent and matrix, which can degrade heat-sensitive compounds. For example, in the study of Lasunon et al. (2021) on the effect of MAE on bioactive compounds from industrial tomato waste, an increase in power from 300 to 450 W resulted in a reduction of around 15% in trans-lycopene, highlighting the vulnerability of carotenoids and phenolic acids to excessive heat. Accordingly, it may be that the phenolic compounds of interest in our DPAAE obtained in the optimal microwaving condition (480 W for 11 min) were degraded. In addition, thermogravimetric analysis (TGA) shows that temperatures in excess of 200 °C trigger the decomposition of organic compounds such as polyphenols and condensed tannins, diminishing antibacterial effects (Khalfi et al., 2024).

Regarding sonication treatment, as reported by Peng et al. (2023), acoustic cavitation disrupts cell walls but can also degrade bioactive compounds. Collapsing bubbles generate hydrodynamic shear that fragments large molecules, as illustrated by a 67% drop in TFC in propolis after 40 min. In pomegranate skin extracts, this phenomenon is reflected in a 20% reduction in *punicalagin* with ultrasounds for 30–50 min. Accordingly, it is probable that the phenolic compounds that were the subject of our DPAAE, which were extracted under optimal sonication conditions (40% amplitude for 60 min), were subjected to degradation. Our findings are in accordance with those of Abdennabi et al. (2017) on MAE of phenolic compounds from date saps and antibacterial activity evaluation against five strains: *Pseudomonas aeruginosa*, *S. aureus*, *E. faecalis*, *Bacillus cereus*, and *Bacillus subtilis*. The sap extract (1 mg/mL) of the *Beser* cultivar showed no bacterial activity. Our recommendations are substantiated by the findings of Sandeep et al. (2023), who discovered that at low concentrations (40 and 60 μL) of *Moringa* extract, the conventional soaking method exhibits a greater inhibition zone compared to the ultrasonic method, as well as the microwave method at higher concentrations (80 and 100 μL).

From a mechanistic point of view, the antibacterial effect observed with the WAE extract and the absences of this effect with extracts obtained by MAE/UAE depend closely on how these techniques modify the stability, solubility, and structural integrity of bioactive compounds. Rapid, intense microwave heating (often $> 80\text{ }^\circ\text{C}$) can break hydrogen bonds and degrade heat-sensitive compounds such as flavonoids and polysaccharides, impairing their ability to inhibit bacterial adhesion by altering interactions with microbial cell walls (Deng et al., 2022 and Bouarab-Chibane et al., 2019). As for sonication, the shear forces generated by cavitation and localized hot spots fragment macromolecules. This process can oxidize certain phenolic acids, reducing their antimicrobial activity (Monadal et al., 2021 and Rahmatia et al., 2023). Aqueous WAE has been shown to be effective in inhibiting *E. coli* growth, although this depends on the plant species and the nature of the bioactive compounds. Its main mechanism of action is to disrupt the bacterial membrane, resulting in the release of intracellular components (nucleic acids and proteins) (Gonelimali et al., 2018). Thus, as highlighted in the study by Bessalah et al. (2023), eight extracts obtained by WAE (50 $^\circ\text{C}$ for 30 min) disrupted the membrane of *E. coli* F17, causing the release of nucleic acids after 12 h of incubation.

In addition, the hydrophobic surface of this strain was modified, and its motility was also altered in the presence of these extracts.

In the specific context, the absence of antibacterial activity of a date extracts obtained by MAE and UAE is desirable or even imperative. Case in point: microbial culture media (Rini et al., 2023). On the other hand, the extract obtained from WAE may serve as a natural food preservative against *E. Coli*: these antimicrobial agents of natural origin constitute a credible alternative to chemical preservatives for the stabilization of highly perishable foods, notably meats and dairy products, effectively limiting the proliferation of *E. coli* and spoilage phenomena (Imran et al., 2021).

4.3. Conclusion

The current study highlights that the choice of aqueous extraction method of total soluble solids from date pulp is determined by the specific objective of the application, with each extract presenting distinct characteristics that influence the quality and properties of the final product. As such, it is essential to evaluate the specific attributes of each method and their potential impact. For instance, the significantly higher concentration of sucrose in the DPAAE produced by WAE (139.12 ± 7.71 mg/mL of DPAAE) indicates that it could be a potential source of refined sugar. Also, both non-conventional methods produced date extracts that are suitable for probiotic formulations against *E. coli* strains. The microwave method stands out for its efficiency in extracting total soluble solids, including total sugars (22.23 ± 0.23 g/100 mL of DPAAE), while maintaining a high colorimetric intensity index ($76.85 \pm 0.46 \times 10^{-3}$) and an increased concentration of phenolic compounds (1.69 ± 0.04 mg GAE/mL of DPAAE), reflecting a remarkable antioxidant capacity (with an IC_{50} of 729.80 ± 12.87 μ g/mL for the methanolic extract). This makes microwave irradiation particularly suitable for the production of antioxidant-enriched date products for consumers seeking health benefits. In addition, this method offers a higher extraction recovery in a shorter time; MAE is three times faster than that required by conventional techniques, making it a promising option for pulp pre-treatment or for use in combination with other techniques to improve material and energy transfer. The aqueous date extract obtained by sonication, rich in glucose (50.86 ± 3.68 mg/mL) and fructose (53.57 ± 4.16 mg/mL), enhances the perception of sweetness in foods.

Thanks to the high sweetness intensity of fructose (1.2–1.7 times that of sucrose) and the moderate but persistent sweetness of glucose (0.7–0.8 times that of sucrose), this extract offers a superior sweetness to sucrose alone. Its balance of glucose and fructose allows less sugar to be added while maintaining optimal sweetness perception, making it an ideal ingredient for dietary products. In addition, ultrasound-assisted extraction is limited in its ability to recover all solid matter from date pulp. Therefore, we recommend further research aimed at optimizing ultrasonic-assisted aqueous extraction (AUAE) to improve the recovery of reducing sugars from this pulp and to evaluate its impact. Regarding the antibacterial effect, since extraction is the first step in obtaining the constituents of medicinal plants, this requires that many factors are taken into account when choosing the most appropriate techniques. The use of appropriate methods guarantees the maximum production of plant compounds in sufficient quantities to perform the required antibacterial tests. We suggest further studies on water bath–assisted aqueous extraction (AWAE) to obtain a natural DPAAE with high antibacterial activity (inhibition zone of 18 ± 2 mm) against *E. coli*. These results encourage the optimization of the production of natural extracts derived from date pulp, promoting their application as both functional and nutritious ingredients and strengthening the development of the date-palm industry.

Chapter 5

Kinetics of concentration and characterization of date syrup: comparative approach

In order to enhance the quality of the syrup obtained from the date-palm fruit "DS", a comparative study was carried out: this research evaluated and compared the efficiency of a concentration method: vacuum assisted evaporation (VAE), in comparison with Open-heating assisted evaporation (OAE). The aim was to analyze and compare their kinetic concentration behavior of date syrup, and to evaluate and compare its biochemical features and antiradical scavenging activity of the two date syrup samples obtained.

5.1. Materials and methods

5.1.1. Plant material

"*Mech Degla*" cultivar of date palm (*Phoenix dactylifera* L.) used in this study was acquired at the "*T'mar*" maturity stage collected from the local market of Biskra region (South-Eastern of Algeria). The fruits were cleaned and depitted before being air-dried using a ventilated oven (Memmert UN 260, Memmert GmbH, Schwabach, Germany) at a temperature of 40°C to a consistent weight before being ground and sieved (200 µm pore diameter) to obtain a fine powder. The powder was then kept at a temperature of -18 °C until it was needed.

5.1.2. Chemicals and reagents

It was from Merck Millipore in Burlington, Massachusetts, USA, that we obtained phenolphthalein, phenol, 3,5-dinitrosalicylic acid, quercetin, aluminum trichloride (anhydrous), and potassium sodium tetrahydrate, as well as 96% sulfuric acid. Ethanol and acetone were purchased from Scharlau (Barcelona, Spain). Folin-Ciocalteu reagent, gallic acid, sodium carbonate, sodium hydroxide methanol, copper sulfate pentahydrate, potassium sulfate, boric acid, methylene blue, methyl red, hydrochloric acid, butylated-hydroxytoluene (BHT), 2,2-diphenyl-1-picrylhydrazyl radical (DPPH), Carrez solutions I and II sodium bisulfite, phenyl-β-D-glucoside, hydroxylamine chloride in pyridine, hexamethyldisilazane (HMDS), trifluoroacetic acid (TFA), heptane, glucose, fructose, sucrose, caffeoylquinic acid, Di-caffeoylquinic acid, coumaroylquinic acid, caffeic acid, coumaric acid, from Sigma Chemical Co (St. Louis, USA). All the utilized chemicals and reagents were of analytical grade.

5.1.3. Date syrup preparation

First, to produce the date pulp aqueous extract, a water condenser was placed on the upper portion of a multimode home microwave (MAXMOS23S, Maxipower, China) that operates at 2450 MHz and has cavity dimensions of 28.1 cm in height, 48.3 cm in length, and 38.7 cm in depth. A mixture of 100 g of date pulp powder and 600 mL of distilled water were then microwave-irradiated at 480 Watt for 11 minutes. The treatment was performed under an alternative rhythm (10 s power on, 5 s power off to prevent super-boiling), then the collected extract was filtered through Whatman filter paper (N° 4). DAPE with TSS_{initial} \approx 14.4 °Brix) was obtained. Evaporation was stopped as soon as the soluble concentration in the sample reached \approx 75°Brix, which is the end-of-treatment criterion.

5.1.3.1. Open-heating Assisted Evaporation (OAE)

As reported by Asghar et al. (2020), the concentration was conducted at atmospheric pressure (open-pan), a hotplate stirrer (V230, F20520163, Velp scientifica, Italy) operating at 50 Hz and 630 Watt, coupled with digital thermoregulator (F208B0063, Velp scientifica, Italy) operating at 50 Hz and 630 watts was used. 550 mL of the DPAAE was subjected to 100 °C, with continuous stirring (100 rpm), until the end of the concentration process (see figure 5.1a).

5.1.3.2. Vacuum Assisted Evaporation (VAE)

Vacuum evaporation was carried out as outlined by Elik et al. (2016), with minor adjustments, using a rotary evaporator (R-114RE B-480, Buchi, Flawil, Switzerland) operating at 50/60 Hz and 1500 Watt, to concentrating 550 mL of DPAAE, at a constant temperature of 45 °C, and vacuum pressure of 100 mbar for 40 min, with stirring speed of 100 rpm (see figure 5.1b).

After each experiment, DS weights were measured for data analysis until usage. Finally, all of the DS samples are kept in storage at 4 °C.

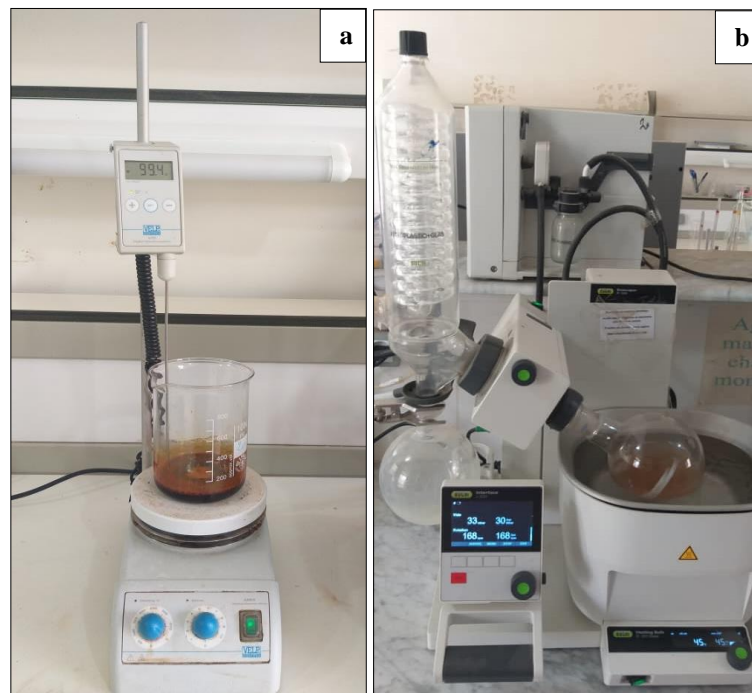


Figure 5.1: DS production by DPAE' concentration using (a) OAE and (b) VAE

5.1.4. Monitoring of temperature and total solid soluble of date syrup during concentration

At regular intervals of 10 minutes for the two methods, the temperature of the boiling DPAE was measured using an electronic thermometer (TP 300, 1.5 V) with a digital temperature indicator that had a range of -10 to 300 °C with a precision of $\pm 0.1^\circ\text{C}$. Also, TSS is measured using three types of hand-held refractometers (Models 0–32, 28–62, and 58–92 °Brix, YIERYI Ltd., China). Each refractometer had a precision of 0.1 °Brix (% w/w).

5.1.5. Kinetic models of concentration

By assessing the change in TSS content, the concentration kinetics of DPAE was examined using the two methods (OAE and VAE). In order to achieve this, the two concentration curves was fitted to the mathematical model of *Henderson and Pabis* (1961), and was evaluated in order to characterize the evolution of TSS concentration over time, with mathematical expressions models is shown in equation 5.1:

$$B - B_0 = a * e^{(-k*t)} \quad (5.1)$$

Where:

B: TSS content at time t (B°); B_0 : initial TSS content (B°); t: concentration time (minute);

a and k : constants

As reported by Terki et al. (2025), the *Henderson and Pabis'* model is a straightforward exponential model that is frequently employed in drying studies to describe the decrease in moisture ratio over time.

5.1.6. Date syrup production yield

Date syrup yield production was calculated according to Al-Hilphy et al. (2023), expressed as a percentage, corresponding to the mass of syrup obtained from 100 grams of processed date flesh, according to the following formula:

$$\text{Production yield (\%)} = \frac{W_{DS}}{W_{DP}} \times 100 \quad (5.2)$$

Where:

- W_{DS} : Weight of date syrup (g);
- W_{DP} Weight of date pulp used (g).

5.1.7. Date syrup' characterization

The two DS samples obtained by applying the optimum values of the two concentration methods (OAE and VAE) were characterized for their functional attributes and biochemical composition.

5.1.7.1. Physicochemical characterization

- pH: (NF V 05-108, 1970) and;
- Titrateable acidity: (NF V05-101, 1974) and;
- TSS: (NF V 05-109, 1970), all were determined in accordance with the protocols described in AFNOR (1984).
- BNE: Non-Enzymatic Browning Index (NEBI): As described by Muñoz et al. (2012).

For the above analysis, as the experimental protocols are identical to those described in chapter 3, only any specific modifications applied in this chapter will be presented.

- Density is determined as described in Farahnaky et al. (2018). The date syrup was subjected to thermal equilibrium at 22°C using a controlled thermostatic enclosure, then the date syrup mass was determined using a precision analytical balance (RADWAG, model AS 220.R2, Poland), while specific volume was measured using a borosilicate glass pycnometer of 50 ml (ISO LAB, 10 ml, BORO 3.3 A, Germany).

The volumic mass, denoted ρ (rho), corresponds to the proportion (ratio) of mass contained in a unit volume of date syrup at 25°C, and is expressed in g/cm³ according to the relationship in equation (5.3).

$$\rho = \frac{m}{V} \quad (5.3)$$

From this value, the actual density (d) of the syrup is determined as the ratio between its density and that of water at the same reference temperature (25°C), where the density of water $\approx 1 \text{ g/cm}^3$. Thus, the actual density is expressed by the formula in equation (5.4), which allows us to evaluate the relative concentration of syrup to water.

$$d = \frac{\rho_{\text{date syrup}}}{\rho_{\text{water}}} \quad (5.4)$$

- 5-hydroxymethylfurfural (HMF) in date extract (DS) is determined as reported by White (1979) (with minor modification), on a UV-Visible spectrophotometric method, based on differential measurement of the absorbance of a clarified aqueous solution at two wavelengths: 284 nm, where HMF exhibits strong absorption, and 336 nm, used as a reference to correct for non-specific interference. A reference solution is prepared by neutralizing the HMF chromophore at 284 nm with sodium bisulfite, enabling a more accurate reading.

To do this, 5 g of sample is dissolved in 25 ml of deionized water, in a 50 ml volumetric flask, then clarified by adding 0.5 ml of Carrez solutions I and II. The volume is made up with deionized water (and a drop of alcohol if necessary), then filtered (discarding the first 10 ml). Two 5-ml aliquots of the filtrate are mixed separately with 5 ml deionized water (sample) and 5 ml 0.20% sodium bisulfite solution (reference), and then homogenized. The absorbance of the sample is measured against the reference at 284 and 336 nm. The HMF content is then calculated according to equation (5.5), and expressed in mg per kg of DS.

$$\text{HMF (mg per 100 g of DS)} = (\text{Abs } 284_{\text{nm}} - \text{Abs } 336_{\text{nm}}) * 14.97 * \frac{5}{W} \quad (5.5)$$

$$\text{The factor } 14.97 = \frac{126 * 1000 * 100}{16830 * 10 * 5}$$

Where:

- 126: Molar mass of HMF (g/mol);
- 16830: The maximum molar absorbance (ϵ) of HMF at $\lambda = 284 \text{ nm}$, expressed as $\text{L. mol}^{-1} \cdot \text{cm}^{-1}$;
- 1000: Conversion factor of gram to milligram;
- 10 : Dilution factor of the date syrup;
- 100: Conversion factor of gram of date syrup to 100 gram;
- W: Weight of the date syrup used (g);
- 5: nominal weight of the date syrup' sample.

5.1.7.2. Biochemical features

- Total ashes (NF V 76-101, 1976) are determined as outlined in (AFNOR, 1984);
- Total sugar content: was assessed using the method of Dubois et al. (1956);
- Reducing sugar content: was measured using the method of Miller (1959).

As the experimental protocols are identical to those described in chapter 3, only any specific modifications applied in this chapter will be presented.

- Total Phenolic amount:

The phenolic extract of our DS is prepared according to Saleh et al. (2011). Phenolic compounds were extracted from DS by combining 10 g with 90 ml of absolute methanol. The mixture is stirred for 30 minutes on a magnetic stirrer at room temperature, and then filtered using Whatman filter paper (N° 4). The residues recovered are then re-extracted three successive times, and re-filtered on büchner funnel under vacuum, lyophilized and stored at -18°C until the analysis. TPC amount is determined according to the method outlined by Agourram et al. (2013), as in chapter 3.

5.1.7.3. Sugar profile determination by GC-MS method

Samples were prepared by diluting 0.1 g date syrup in 5 mL 80% ethanol. A 0.1 mL aliquot of the diluted DS was then transferred to an Eppendorf tube, where 0.25 mL of the internal standard (Phenyl Beta Glucoside) (1mg/mL), was added, then vacuum dried overnight. As previously described by Ruiz-Matute et al. (2010), DS samples were analyzed by GC-MS for sucrose, glucose, and fructose. As the experimental protocols are identical to those described in chapter 3, only any specific modifications applied in this chapter will be presented.

5.1.7.4. Phenolic profile of DS by HPLC-UV

The chromatographic analysis of the phenolic extract was performed according to El-Hawary et al. (2020), with minor adjustments. The instrument used was a Perkin Elmer 200 series HPLC. Compounds were separated on a C18 column. The mobile phase was prepared by combining phase A (95% water) and phase B (5% methanol). Elution conditions were optimized with a flow rate of 1 mL/min and an injection volume of 15 μL . Detection was carried out using a UV-visible detector set at 320 nm. Compounds were identified on the basis of their absorption spectra and retention times using three phenolic standards: caffeoylquinic acid, Di-caffeoylquinic acid, and coumaroylquinic acid.

5.1.7.5. Antiradical scavenging activity

Following a slightly modified version of the procedure described by Braca et al. (2002); as the experimental protocols are identical to those described in chapter 3, only any specific modifications applied in this chapter will be presented.

5.1.8. Statistical analysis

All data were analyzed using Minitab Software (Inc. version 17.1.0). The statistical significance differences between mean values and significant test relative to the effect of the two concentration method (OAE and VAC) on the biochemical features of the three DS samples, were performed using one way analyze of variance (ANOVA) followed by Tukey's HSD (honestly significant difference) test of multiple comparison. P-value of less than 0.05 was used to determine the statistical significance level. The mean \pm standard deviation (SD) was used to express the results.

The mathematical model's constants were estimated using Minitab Software (Inc. version 17.1.0) through Non-Linear Regressions (NLR), based on three statistical parameters: The coefficient of determination (R^2), the reduced chi square values (χ^2) and the root mean quadratic errors (RMSE) or standard deviation of residuals (S), calculated to evaluate the accuracy and performance of the applied models, using equation (5.6, 5.7, and 5.8), respectively:

$$R^2 = 1 - \frac{SST}{SSE} \quad (5.6)$$

$$\chi^2_{reduced} = MSE = \frac{SSE}{n-p} \quad (5.7)$$

$$RMSE = S = \sqrt{\chi^2_{reduced}} = \sqrt{\frac{SSE}{n-p}} \quad (5.8)$$

Where:

SST: Total sum of square; SSE: Residual square error; n: the number of experimental points, and p: number of estimated parameters of the mathematic model (here a and k).

5.2. Results and discussion

5.2.1. Time-temperature and time-TSS profiles during concentration process

The two curves a and b in the figure 2 illustrate the temperature and TSS profiles during concentration of DPAE samples, using the two different methods for OAE and VAE respectively. An in-depth analysis of the two curves reveals distinct dynamics:

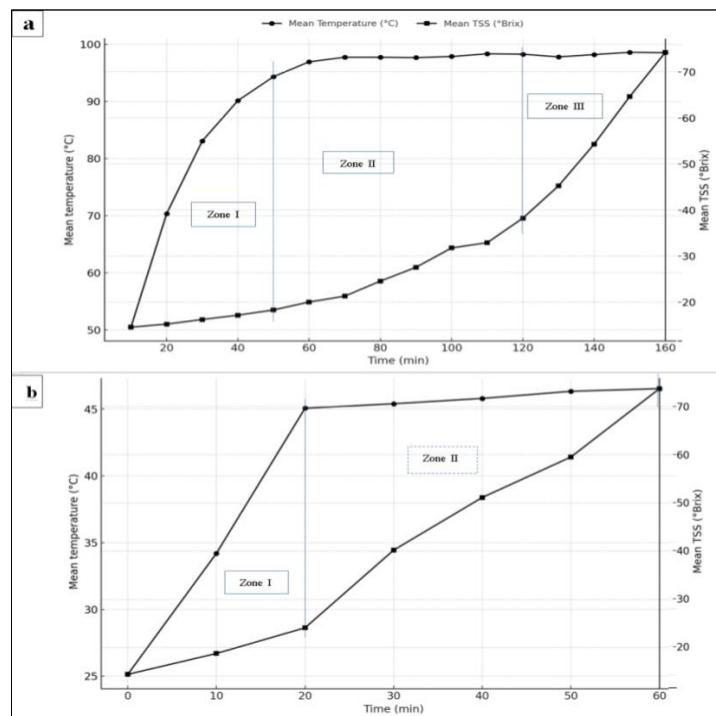


Figure 5.2: Time-temperature and time-TSS profiles of DPAE during syrup manufacturing process (a) OAE , and (b) VAE, error bars show \pm SE, with $n = 3$

Both profiles show similar behavior, with distinct variations in the critical zones. In the OAE method, the evolution of temperature and soluble solids concentration follows three distinct phases:

In zone I (stagnation region), the DPAE temperature rises rapidly until it reaches boiling point around 94°C after 50 minutes. This phase is characterized by a rapid initial rise in temperature, while the increase in TSS remains limited (around 14 to 18.27 ± 0.31 °Brix), due to the fact that the DPAE is still in the preliminary heating phase and has not yet reached its boiling point, which restricts the effective concentration of soluble solids. In zone II (primary evaporation stage), the temperature continues to rise, but more slowly (from around 94 to 98°C), due to the progressive accumulation of soluble solids (up to 38 °Brix). This more gradual increase is due to water evaporation, which results in a higher concentration of solids in the solution. Finally, in zone III (final evaporation stage), there is a rapid rise in mean TSS (from 38.2 to 74.2 °Brix), accompanied by a very moderate increase in mean boiling point (from 98.27 to 98.53°C). This acceleration of the process is due to a reduction in the volume of liquid in the boiling pan, which intensifies evaporation. This phase is critical to the manufacture of date syrup, as it determines its final texture and soluble solids concentration. Precise control of the parameters in this phase is essential to guarantee optimum quality of the final product.

Following the same trends, Jagannadha Rao et al. (2009) reported that the jaggery boiling process can be divided into three zones: the first zone is characterized by a rise in boiling temperature, the second zone is characterized by a gradual rise in temperature and TSS, and the third zone is characterized by a rapid increase in boiling temperature, viscosity, and TSS. In the third zone, the variations were observed in the range of 105-121°C, 4.5 to 988 mPas, and 54.6 to 81.9 (% w/w). In other study conducted by Elik et al. (2016) found that open-pan blackberry (*Vaccinium corymbosum*) juice evaporation at 77 minutes yielded 65 °Brix and 72.35 °Brix at 80 minutes. In contrast, the VAE profile showed moderate variations, with precise temperature control and more delicate evaporation in zone II (final evaporation stage, approximately 46°C), to achieving 73.73 °Brix in 60 minutes. Compared with the result test of Vangapandu & Bitra (2023), using a rotary evaporator under vacuum at 70°C and 550 mmHg (733 mbar), the TSS of guava juice progresses more slowly: 20 °Brix in 150 minutes, 60 °Brix in 300 minutes, then a rapid rise to 65 °Brix. This longer duration can be attributed to a higher operating pressure (733 mbar) than that used in our study (100 mbar). On the other hand, Kuruba et al. (2021) team for Sugarcane (*Saccharum officinarum*) syrup production, achieved 70.5 % w/w, using vacuum pan at 110 °C and 700 mmHg (933 mbar) after 100 minutes, and peaked 83 % w/w at 110 °C and 600 mmHg (800 mbar), and significantly changed with pressure. This pressure difference results in a higher boiling point, which may compromise the precision of concentration parameter control, particularly with regard to thermal stability and evaporation kinetics in the rotary evaporator process; as agrees by Icier et al. (2024) and Venkatesan et al. (2024), the time necessary to achieve the desirable TSS of fruit syrup is significantly influenced by concentration parameters, including temperature and pressure, which directly affect the evaporation rate and process efficiency.

Table 5.1 shows the specific values of boiling temperatures and TSS in Zones II and III, providing a quantitative overview of these essential process control variations.

Table 5.1. Recap of time, boiling temperature ranges and TSS concentrations for both concentration methods

	Concentration method Parameters	OAE	VAE
Zone I	Time (min)	0 – 50	0 – 20
	Boiling temperature (°C)	23 – 94.33±0.31	25.13±0.12 – 45.07±0.12
	TSS (°Brix)	14.4 – 18.27±0.31	14.4 – 24.07±0.46
Zone II	Time (min)	50 – 120	20 – 60
	Boiling temperature (°C)	94.33±0.31– 98.27±0.31	45.07±0.12 – 46.53±0.31
	TSS (°Brix)	18.27±0.31– 38.20±0.72	24.07±0.46 – 73.73±0.50
Zone III	Time (min)	120 – 160	
	Boiling temperature (°C)	98.27±0.31– 98.53±0.12	
	TSS (°Brix)	40.87±0.61– 74.2±0.53	

Data shown were mean ± SD of three replications (n=3)

As presented in figure 5.3, prolonged evaporation of the DPAE at elevated temperature above 100°C enhances Maillard reactions resulting in the formation of a dark DS, a sought-after characteristic in the preparation of traditional meals (Almuziree & Alhomaïd, 2023).

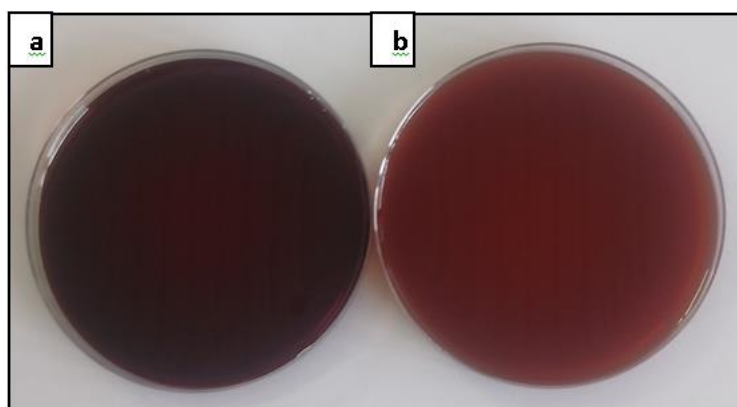


Figure 5.3: Date syrup (DS) samples obtained by applying the concentration method from left to right a) OAE and b) VAE

5.2.2. Mathematical modelling of concentration kinetics

Numerous researchers have highlighted the benefits of mathematical models for a better understanding and control of the parameters involved in a dehydration or concentration process. (Dinçer et al., 2019). Mathematical models are invaluable tools for gaining an in-depth understanding of the transport phenomena involved in processing, and for controlling or optimizing the various process variables (Rasmuson et al., 2014).

Due to its dense, rich composition, date juice reacts more intensely than other tropical juices to increases in total soluble solids (TSS). The marked rise in viscosity and density, coupled

with the drastic drop in thermal conductivity and specific heat, makes it a fluid with complex behavior (Jagannadha Rao et al., 2009), requiring specific technological management during heat treatment, concentration or storage. These physicochemical properties play a decisive role in energy and matter transfer phenomena.

In this context, the concentration process can be modeled using theoretical, semi-theoretical or empirical equations, generally based on the overall heat transfer coefficient, which is strongly influenced by the inner film transfer coefficient. The latter depends on a number of factors, including the physical properties of the fluid - such as viscosity, density, specific heat or thermal conductivity - as well as the flow regime (Ramírez & Ruiz, 2021). Thus, any variation in these properties, as observed in date juice when enriched with TSS, directly affects the thermal efficiency of the process and must be rigorously taken into account when designing unit operations.

Although several researchers have described the dehydration or concentration of food products using models such as that of *Henderson and Pabis*, there is still a gap in the literature regarding the application of these models to date juice concentration. The *Henderson and Pabis* model is a simple exponential model describing the increase in Brix degree over time, often applied in juice concentration studies (Terki et al., 2025).

The following equation (5.9) and (5.10) represent the mathematic model of *Henderson and Pabis predicted* for the date extract concentration using OAE and VAE, respectively:

$$B - B_0 \exp = 1.49741 * \exp^{(0.0232274 * \text{Time})} \quad (5.9)$$

$$B - B_0 \exp = 6.77198 * \exp^{(0.0371384 * \text{Time})} \quad (5.10)$$

Table 5.2 presents the coefficient of determination (R^2), the Reduced Chi Square (χ^2) or Mean Squared Error (MSE), and the Root Mean Squared Error (RMSE) or Standard deviation of the model (S), calculated to evaluate the accuracy and performance of the applied models.

The *Henderson and Pabis* distribution fit well into the kinetic behavior of concentrating date extract, for the two concentration methods, as its curves tended to fit well, and the R^2 , RMSE, and RMSE values are significative (Table 5.2).

Table 5.2: Values of the kinetic constants obtained from the *Henderson and Pabis* model, with the results of the associated statistical analysis

Concentration method	Model coefficients		Statistical parameters		
	a	k (-)	R^2	χ^2	RMSE
OAE	1.49741	0.02323	0.995	1.661	1.289
VAE	6.77198	0.03714	0.938	37.123	6.092

The mathematical model for OAE and VAE curves are shown in Figure 5.4,a and 5.4b, respectively. With increasing evaporating temperature, the simulation's efficacy offered by the model improved. Chua & Leong (2020) also observed comparable results for the *Henderson and Pabis* model for the concentration of pineapple juice by microwave heating.

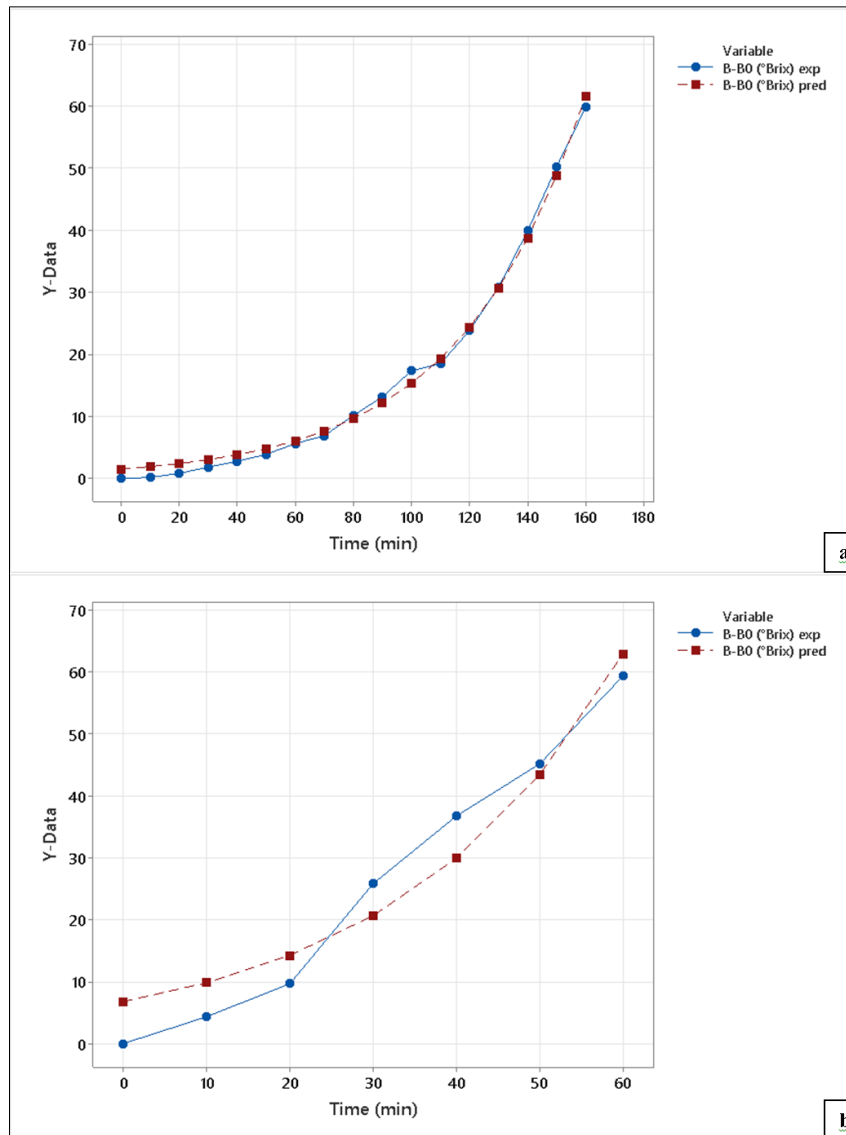


Figure 5.4: Experimental and predicted values for variation in TSS content (° Brix) for OAE (a), and VAE (b)

This Figure 5.5 highlights the increased efficiency of the VAE method in concentrating date extracts more rapidly than the OAE method, while achieving comparable levels of TSS. This suggests that the VAE method is more time- and potentially energy-efficient.

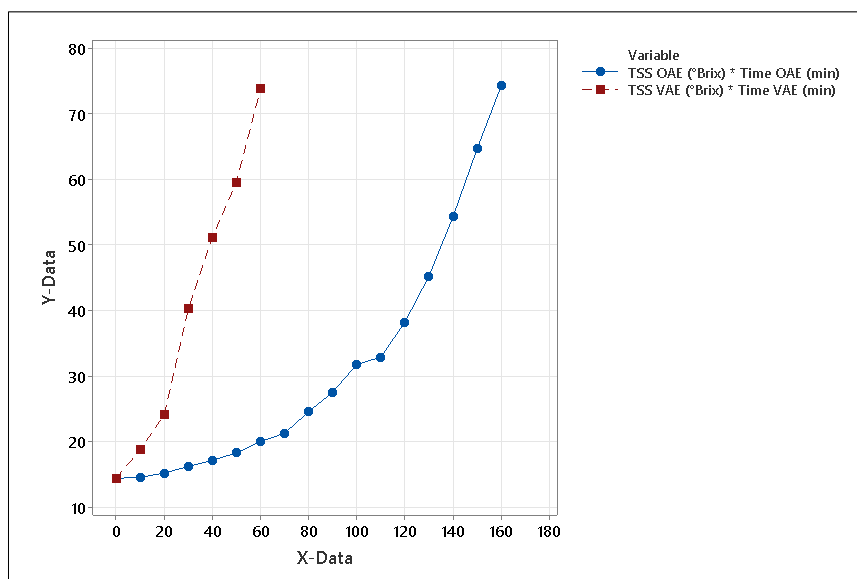


Figure 5.5: The variation of TSS amount over time of the date extract using the two evaporation methods OAE and VAE

5.2.3. Comparison of the production yield, concentration methods in term of their effect on physicochemical features of the date syrup

No significant difference was observed in the production yield of date syrup, with values of $33.16 \pm 0.43\%$ under OAE, compared to $32.41 \pm 0.21\%$ under VAE (figure 5.6).

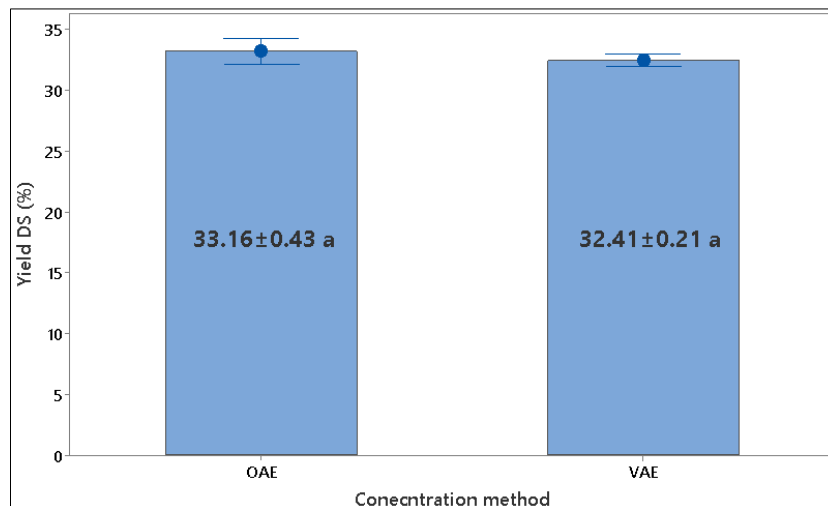


Figure 5.6: date syrup production yield using the two evaporation methods OAE and VAE

In our study, two methods were used to concentrate the date extract. OAE method achieved an efficiency of $33.16 \pm 0.43\%$ by heating at 100°C with continuous stirring (100 rpm) on a 630W hot plate, under atmospheric pressure. VAE method yielded $32.41 \pm 0.21\%$, using a rotary evaporator at 45°C , under vacuum at 100 mbar for 60 minutes, with the same stirring speed.

In the study by Al-Hilphy et al. (2012), using an Iraqi variety “*Shukri*”, ohmic heating “OH” was performed under vacuum at a pressure of 0.8 bar, with a power of 60 W, produced a significantly higher yield of $60.93 \pm 3.76\%$, highlighting the efficiency of this technique by minimizing thermal losses and optimizing evaporation. In comparison, their conventional “CH” vacuum heating method (also at 0.8 bar) achieved an efficiency of $35.43 \pm 2.99\%$, slightly higher than our results, by heating a water-date mixture (1:1.5) boiling, followed by filtration and evaporation of up to 72% soluble solids.

Julai et al. (2023), using the “*Barhi*” variety, had a lower yield of between 25 and 30%. They were evaporated over an open fire at 95°C for 3 hours with constant stirring. In parallel, vacuum evaporation was carried out at 50°C and 16 kPa for 25 minutes using a rotary evaporator.

The table 5.3 below presents the main functional and biochemical characteristics of both date syrups as they are influenced by the two concentration methods used.

Table 5.3: The most important functional characteristics and biochemical features of the two date syrup (DS) as affected by the two concentration methods

Concentration method	OAE	VAE
Characteristics		
Functional characteristics		
pH	5.19 ± 0.16^a	5.45 ± 0.08^a
Total soluble solids (TSS) (% FW)	74.2 ± 0.53^a	73.73 ± 0.50^a
Non-Enzymatic Browning Index (NEBI)	0.81 ± 0.07^a	0.58 ± 0.09^b
Density (g/cm^3)	1.36^a	1.33^a
HMF ($\text{mg}/100 \text{ g FW}$)	10.40 ± 0.98^a	8.05 ± 0.44^b
Biochemical features		
Moisture (%)	21.22 ± 4.74^a	22.38 ± 7.77^a
Total ash (% FW)	2.34 ± 0.10^a	2.23 ± 0.19^a
Titrate acidity (g of citric acid eq. /100 g FW)	1.4 ± 0.056^a	1.10 ± 0.06^b
Total phenolic content (TPC) ($\text{mg GAE}/\text{g FW}$)	4.51 ± 0.38^b	6.42 ± 0.80^a
Total sugar (% FW)	72.57 ± 7.42^b	87.30 ± 3.46^a
Reducing sugar (% FW)	44.47 ± 6.589^a	18.31 ± 4.14^b
Sucrose (% FW)	26.56 ± 4.46^b	68.05 ± 5^a
Glucose (% FW)	21.66 ± 1.56^a	7.83 ± 0.34^b
Fructose (% FW)	21.28 ± 1.78^a	8.36 ± 0.3^b
Fructose/glucose ratio	0.98 ± 1.14^b	1.06 ± 0.89^a

Data shown were mean \pm SD of three replications (n=3); the superscripts **a** and **b** after the mean \pm SD values indicate significant differences according to the Tukey test. Values with different letters within the same line are significantly different at $P < 0.05$

- *pH and titratable acidity*

In liquid matrices such as date syrups, pH and titratable acidity are closely related, but provide complementary information: pH reflects the concentration of free H⁺ ions in solution, while titratable acidity measures the total amount of available acids, including those bound or weakly dissociated. In our study, the concentrated syrup on open-heating has a lower pH (5.19 ± 0.16) and a higher titratable acidity (1.40 ± 0.056 g citric acid/100 g FW) than that obtained under vacuum (pH 5.45 ± 0.08 , acidity 1.10 ± 0.06 g/100 g FW). This inverse relationship confirms that increasing overall acidity results in greater release of H⁺ ions, thereby lowering pH.

This trend is consistent with the observations of Ganbi et al. (2012) who report syrups with lower pH (4.53-4.87) also exhibiting higher titratable acidity (1.3-1.59 mg/100 g FW), compared with vacuum syrups (pH 4.96-5.31 and acidity 1.03-1.24 mg/100 g FW). Similarly, Julai et al. (2023) noted a lower pH (4.60 ± 0.13) for higher measured acidities (up to 1.65 g/100 g FP). Conversely, El-Nagga et al. (2012) record a high pH (6.30) associated with a lower acetic acidity (5.99 mg/100 g PF), illustrating the impact of acid type (citric vs. acetic) and date variety (*Saidy* vs. *Mech Degla*) on the pH/acidity relationship.

In conclusion, the comparison of our data with the literature highlights that the concentration method, date variety and type of majority acid simultaneously influence pH and titratable acidity. For a better understanding of the organoleptic quality and microbiological stability of syrups, it is essential to analyze these two parameters jointly, and to standardize methods of expression (fresh weight vs. dry matter) and measurement (type of acid).

- *TSS, density and moisture*

In date syrups, TSS, density and moisture content form an intrinsically linked triptych: a high TSS implies an increased concentration of solids, which translates into a higher density and, correlatively, lower moisture content. In our study, in both OAE and VAE samples, we observed that a slight drop in TSS under vacuum was accompanied by a decrease in density and a slight increase in moisture, confirming the sensitivity of these parameters to pressure and temperature conditions.

Ganbi et al (2012) extracted the juice using magnetic agitation, enzymes and ultrasound, before concentrating it in open air and then under vacuum ($60 \pm 5^\circ\text{C}$, 500-600 mmHg). The syrups thus obtained had an average TSS of 77.8 g/100 g FW, a density of 1.32 g/cm³ and a moisture content of 23.44%, values close to those obtained in our study with vacuum concentration (VAE). For their part, Negga et al (2012) used microwave extraction followed

by vacuum concentration at 70°C, achieving a TSS of 75.11 % FW and moisture reduced to 20.89 %, confirming the significant influence of concentration temperature on water evaporation efficiency.

In our study, concentration on a hot plate at 100°C (OAE) achieved a density of 1.36 g/cm³. In comparison, Helmy et al (2023), combining microwave extraction with prolonged concentration on a plate at 80 ± 5°C for 5 hours, achieved a significantly higher density (1.61 g/cm³), reflecting further water evaporation due to the extended treatment time.

Finally, El-Samahy et al (2009) applied a process combining high pressure and high temperature (5-10 bar, 85-170°C), followed by thin-film evaporation at 67°C (up to 72.5 °Brix). This process yielded a TSS of 72.5 g/100 g FW, a density of 1.357 g/cm³ and a moisture content of 23.52%. These values are still slightly lower than those obtained with our OAE method, probably due to the longer evaporation time (105 minutes), which favored a gentler but effective concentration.

- *HMF and non-enzymatic browning index*

Joint evaluation of the NEBI and 5-hydroxymethylfurfural provides a better understanding of the impact of concentration methods on date syrup quality. In our study, both parameters show a consistent trend: higher values were recorded with the “OAE”, with a NEBI of 0.81 ± 0.07 and an HMF content of 10.40 ± 0.98 mg/100 g FW), while the vacuum method lowered these values to 0.58 ± 0.09 and 8.05 ± 0.44 mg/100 g FW respectively.

These results suggest a direct correlation between the intensity of non-enzymatic browning and HMF formation. HMF is a well-known marker of Maillard reactions and thermal browning. Concentration on a hot plate at 100°C in our study favored increased formation of browning compounds, in contrast to concentration under vacuum, carried out at a more moderate temperature, which limits thermal degradation.

Helmy et al (2023), who applied a prolonged hot-plate concentration at 80 ± 5°C for 5 hours, report a lower NEBI value (0.551) but a very high HMF content (24.0 mg/100 g FW). This contrast could be explained by the prolonged processing time, which favors the thermal degradation of sugars and the accumulation of HMF, even if visual browning (reflected by NEBI) remains moderate. This indicates that NEBI and HMF, although closely related, are not always proportional and may respond differently to certain processing conditions.

This increase in HMF in OAE syrup reflects a higher thermal intensity, favorable to the degradation of sugars, and thus to the formation of colored neo-formed products, which contribute directly to the darkening of the final product. These results are consistent with the

mechanisms described in the literature, as Abbès, et al. (2013), where the elevated correlation coefficient may result from the concurrent creation and intensification of brown pigment during non-enzymatic browning and the synthesis of HMF chemical in heat-treated sweet products.

Acrylamide ($\text{CH}_2=\text{CHC}(\text{O})\text{NH}_2$), a conjugated molecule generated accidentally during heating process of plant foods, is a toxic molecule known for its carcinogenic and neurotoxic potential contaminant. It was not quantified in this study, it should be pointed out that this compound, like HMF, is a neo-formed product generated during heat treatments involving reducing sugars and amino acids. Several studies, notably those by Bahrami et al (2021), agreeing that, acrylamide can be formed in date products requiring heat treatment, such as date syrup. Thus, the significant rise in HMF levels we observed, particularly in the OAE process, could also reflect a parallel formation of acrylamide, although this cannot be asserted without specific analysis. This potential correlation justifies future targeted investigations into this contaminant in date syrups.

On the sensory front, the study by Al-Belushi et al (2021) of Pakistani consumers' preferences for date syrup showed a marked preference for a low-sugar taste, and a medium to dark brown color, considered more natural and attractive.

Although our study did not include sensory analysis or preference testing with Algerian consumers, it may be relevant to draw on data from other cultural contexts to consider the organoleptic implications of our findings. In this respect, the study by Al-Belushi et al (2021), carried out among Pakistani consumers, showed that sensory preferences for date syrup tend more towards a product with low sugar content, medium to dark brown in color. In our study, the syrup obtained using the OAE process had a darker hue than that obtained using VAE, which could, by analogy, correspond to similar preferences in other populations. However, in the absence of data specific to the Algerian population, any extrapolation must remain cautious, and future targeted sensory investigations would be necessary to validate these hypotheses in a local context.

- *Ash*

Analysis of the total ash content of date syrups obtained using different concentration methods reveals significant variations depending on the method used and the variety of dates processed. In our study, carried out on the “*Mech Degla*” variety with a dry consistency, the values obtained were $2.34 \pm 0.10\%$ FW for OAE and $2.23 \pm 0.19\%$ FW for vacuum concentration. These results show no significant difference between the two methods according to Tukey's test, indicating similar mineral preservation.

Comparatively, Ganbi (2012), working on the soft variety “*Nabtat Sultan*”, reported an ash content of 1.75% with the hot plate method and 2.325% in vacuum concentration. This increase under vacuum conditions may be attributed to better mineral preservation due to gentler evaporation. Similarly, Negga et al (2012), using a semi-dry variety “*Saidy*”, obtained a value of 1.82% under vacuum, confirming the influence of variety and concentration method.

Julai et al (2023), using an innovative evaporation process based on ohmic heating (OH) under vacuum for the “*Shukri*” variety, obtained a value of 2.51%, the highest among the studies compared. This result suggests that ohmic heating may enable enhanced mineral preservation, possibly due to uniform heating and reduced processing time that limits the loss of sensitive compounds.

- *Sugars*

Variations in DS sugar composition result from the thermodynamic conditions specific to each process, as affirmed by Makhoul-Gafsi et al. (2018) which this study examined the combined impact of ultrafiltration and thermal variation on the characteristics of syrups made from sap.

Evaluation of the total sugar content of date syrups reveals the significant influence of the concentration method and the date variety used. In our study, concentration under vacuum resulted in an average total sugar content of 87.30 ± 3.46 g/100 g FW, significantly higher than that observed for open heating method, which was 72.57 ± 7.42 g/100 g FW. This difference could be linked to better preservation of sugars under vacuum, due to more moderate thermal exposure.

Similar results were observed by Negga et al. (2012) and Julai et al. (2023), with contents reaching 87.48 and 90.11 g/100 g FW respectively under vacuum. In contrast, lower levels of total sugars were reported by Negga et al. (2012) (69.25 g/100 g FW) and El-Samahy et al. (2009) (67.17 g/100 g FW) using the vacuum method. These values probably reflect increased thermal degradation of sugars, accentuated by high temperatures and prolonged processing times (105 min).

With regard to reducing sugars, the trend is reversed in our study. Concentration OAE led to a significantly higher content (44.47 ± 6.59 g/100 g FW) than the vacuum (18.31 ± 4.14 g/100 g FW). This could be explained by thermal hydrolysis of non-reducing sugars under the effect of higher temperatures, favoring conversion to reducing sugars. However, significantly higher values were obtained in other studies, notably by Assous et al. (2014) with 86.34 g/100 g FW

for vacuum (100 mmHg) at 70°C, and 86.32 g/100 g FW by open-pan method at elevated temperature (100°C), highlighting the influence of processing conditions, pH and variety.

One fructose and one glucose monomer constitute sucrose. Thus, an open system in OAE with prolonged heating at high temperature favors partial hydrolysis into equimolar combination of sucrose into glucose and fructose (Table 5.3), but without causing any major imbalance between these sugars (Cotte et al., 2004).

VAE, operating at low temperature under vacuum, preserves more sucrose (68.05 ± 5 % FW), indicating more effective preservation of this disaccharide under reduced-temperature processing conditions. The use of vacuum evaporation in DS production offers a significant advantage over conventional evaporation at atmospheric pressure for saccharide preservation and enrichment. Sucrose, derived from sugar cane and sugar beets, benefits from advanced separation and purifying methods such vacuum evaporation. This method, along with membrane distillation, efficiently removes residual water and yields high-purity concentrates (Li et al., 2021). In this context, Muwanika (2017) even estimated the loss of sucrose due to the inversion reaction following multiple-effect evaporation, during sucrose processing from sugarcane (*Saccharum officinarum*).

The almost equimolar glucose and fructose composition of our two date syrups allows them to be used as sweeteners alongside other sweetening alternatives such as honey, molasses, as well as refined sugar, brown sugar and maple syrup, which have similar compositional profiles despite their varied forms and origins (Latulippe & Skoog, 2011). In addition, the fructose/glucose ratio remains relatively close to 1 in both DS (0.98 ± 1.14 for OAE and 1.06 ± 0.89 for VAE), bringing them closer to natural sweeteners such as honey and maple syrup, characterized by comparable ratios. Therefore, as affirmed by Shepherd & Gibson (2006), these results suggest that, despite differences in the absolute concentration of sugars, our date syrups obtained retain a similar balance between fructose and glucose. In the context of fructose malabsorption, they may not enhance the risk of malabsorption compared to other natural sweeteners like high-fructose corn syrup. Further date syrup digestibility and metabolic response investigations are needed to confirm this notion.

Note that the syrup obtained by OAE, due to the high fructose content (21.28 ± 1.78 % FW), surpassing that of the syrup obtained by VAE (8.36 ± 0.3 % FW). This makes it particularly interesting for pastries and baked goods, where it improves moisture retention and prolongs freshness (Dana & Sonia, 2024).

The corresponding GC-MS chromatograms of the sugar profile of the DS obtained by OAE and VAE methods were presented in figures 5.7a and 5.7b, respectively.

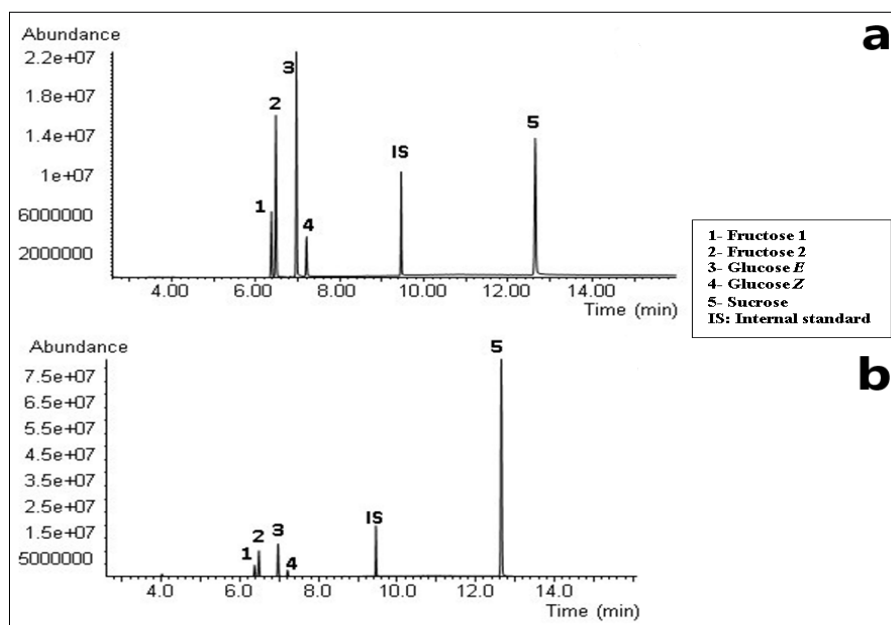


Figure 5.7. GC-MS chromatograms of the two date syrup samples as obtained by (a) OAE and (b) VAE

- 1: D-Fructose, 1, 3, 4, 5, 6-pentakis-O-(trimethylsilyl)-,O-methyloxime(1); RT = 6.36 min.
 2: D-Fructose, 1,3,4,5,6-pentakis-O-(trimethylsilyl)-,O-methyloxime(2); RT = 6.47 min.
 3: D-Glucose, 2, 3, 4, 5, 6-pentakis-O-(trimethylsilyl)-, O-methyloxime (syn); RT = 6.96 min.
 4: D-Glucose, 2, 3, 4, 5, 6-pentakis-O-(trimethylsilyl)-, O-methyloxime (anti); RT = 7.20 min.
 5: Sucrose, α -D-Glucopyranoside, 1, 3, 4, 6-tetrakis-O-(trimethylsilyl)— β -D fructofuranosyl—2, 3, 4, 6-tetrakis-O-(trimethylsilyl); RT = 12.63 min.
 IS: Internal standard: phenyl- β -glucopyranoside; RT = 9.45 min.

The GC-MS method offers an effective approach for the qualitative and quantitative analysis of a wide variety of sugars, including monosaccharides (glucose, fructose) and disaccharides (sucrose), thanks to its enhanced flexibility and sensitivity (Guadalupe et al., 2012). To optimize their detection, reducing sugars are first converted to TMS-oximes, while non-reducing sugars such as sucrose undergo only silylation (Ratsimba et al., 1999). This essential step improves their volatility and stability, making them easier to detect (Faraco et al., 2016). The use of mass spectrometry then enables fine separation and sensitive detection, even at low concentrations (Wahjudi et al., 2010). Our chromatograms show, among other things, the presence of syn and anti isomers of fructose and glucose, as well as sucrose and IS (blank pyridine). Finally, parameters such as sample type, operating conditions or sugar stereochemistry significantly influence retention times (Whitney et al., 2007; Kranenburg et al., 2019).

5.2.4. HPLC-UV Phenolic compound quantification

Chromatographic analysis of phenolic compounds in DSs obtained by two different concentration methods revealed significant differences in the profiles and concentrations of the phenolic compounds identified (figure 5.8 and table 5.4). The temperature and pressure used to evaporate the aqueous extract appear to have a significant impact on polyphenol preservation and transformation.

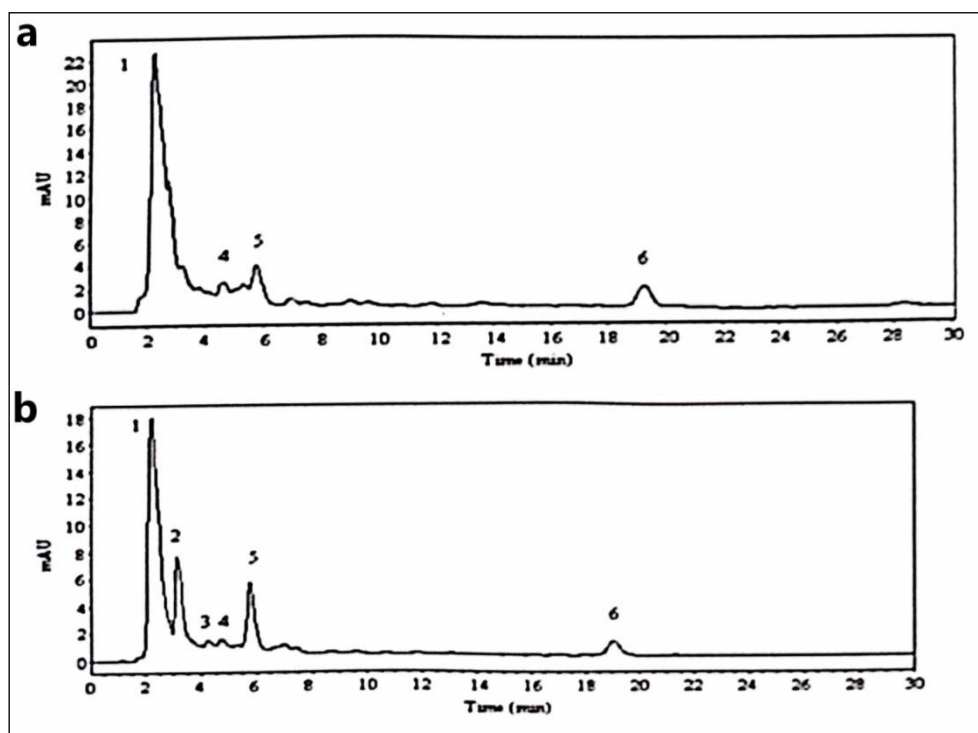


Figure 5.8. HPLC-UV chromatogram of the two rich phenolic extract of date syrup obtained by the two concentration method a) OAE and b) VAE

Table 5.4: Concentration of phenolic compounds presents in the rich phenolic extract of date syrup obtained by the two concentration method OAE and VAE

N° Peak	Rt (min)	Compound name	Concentration (mg/mL)	
			OAE	VAE
1	2.2	5-O-trans-caffeoylquinic acid	50.01	43.8
2	3.1	5-O-cis-caffeoylquinic acid	0	4.43
3	4.2	Di-caffeoylquinic acid	0	0.13
4	5.2	Not identified	/	/
5	6.1	O-p-coumaroylquinic acid	1.2	2.31
6	19.3	Not identified	/	/

Phenolic compounds founded in our DS samples belong to the hydroxycinnamic acid subclass, which represents the most predominant phenolic acids in plant matrices, and exhibit significant commercial value, as reported by Kumar & Goel (2019) and Da Silva et al. (2023).

Paralleled, recent advances in hydroxycinnamic acids highlight their beneficial role for human health Fernández-Jalao et al. (2019) and (Coman & Vodnar, 2020). On the other hand, several investigation as Hirth et al. (2015) and Bonilla et al. (2024), confirm that the stability of hydroxycinnamic acids is affected by thermal food process parameters.

5-O-trans-caffeoylquinic acid was in the majority in both DSs, with a higher concentration in the syrup concentrated at 100°C (50.01 mg/mL vs. 43.8 mg/mL at 45°C). In contrast, the 5-O-cis-caffeoylquinic form, absent at 100°C, is slightly preserved at 45°C (4.43 mg/mL). Thus, high temperature favors stereo-isomerism of the *Cis* form to *Trans*. In this context, Dawidowicz & Typek (2010), report that caffeoylquin derivatives undergo isomeric rearrangements under different heating conditions. Therefore, in general, all-trans-isomers have the highest bioactivity and cis-isomers the lowest (Shi et al., 1999). Based on those statements, isomerization can increase 5-O-trans-caffeoylquinic acid bioactivity in our open-heat-assisted evaporation date syrup.

Di-caffeoylquinic acid is only detected in VAE' DS, albeit at a very low concentration (0.13 mg/mL). The absence in OAE' sample may be explained by increased thermal sensitivity, potentially leading to degradation during concentration at high temperature. In this light, in his study on the effects of cooking methods on phenolic acids concentration in sweet potato, Kurata and his research team (2019) found that boiling significantly reduces 4,5-di-O-caffeoylquinic acid and 3,5-di-O-caffeoylquinic acid. On the other hand, steaming and frying increase 3,4-di-O-caffeoylquinic acid content, while boiling reduces it.

O-q-coumaroylquinic acid is present in both DS, but in higher concentration in VAE sample (2.31 mg/mL) than in OAE sample (1.2 mg/mL). This result may suggest better preservation of sensitive compounds during low-temperature vacuum concentration. In addition, the aglycone of O-p-coumaroylquinic acid, namely p-coumaric acid, was identified in the methanolic extract of date palm jelly and date palm nectar by Hoffmann et al. (2017).

5.2.5 Total phenolic content and antiradical scavenging activity

Analysis of the total phenolic compound content in date syrups (table 5.3) enables us to assess the effect of concentration methods on the preservation of bioactive compounds. In our study, VAE yielded a significantly higher TPC content (6.42 ± 0.80 mg GAE/g FW) compared to OAE, which generated a value of 4.51 ± 0.38 mg GAE/g FW. This statistically significant difference ($p < 0.05$) highlights the protective effect of vacuum treatment against thermal degradation of phenolic compounds.

In comparison, Ganbi (2012) obtained lower values, with 1.698 mg GAE/g under open heating and 1.868 mg GAE/g under vacuum, despite the use of advanced extraction techniques such as enzymatic and ultrasonic extraction. This could be explained by the nature of the variety used (*Nabtat Sultan*, soft consistency).

The results of Negga et al (2012) (1.65 mg GAE/g), Helmy et al (2023) (2.886 mg GAE/g), and Assous et al (2014) (3.6834 mg GAE/g in open heating and 4.2474 mg GAE/g under vacuum) confirm the impact of the concentration method. Moderate-temperature processes under vacuum appear to preserve phenols to a greater extent than open-system methods at elevated temperatures. Assous et al. (2014), in particular, show a clear improvement in CPT using the rotary evaporator compared to the open pan.

Al-Farsi et al. (2007), studying Omani varieties, reported values ranging from 0.96 to 1.62 mg GAE/g, the lowest overall. This may be due to the combination of aqueous extraction at 60°C and concentration at a higher temperature (70°C), which could result in partial phenol degradation.

The phenolic structure of these compounds gives them enhanced antioxidant properties, including the ability to scavenge DPPH radicals (Villaño et al., 2007). Al-Mamary's study (2014), using Vit. C as a standard antioxidant compound demonstrated that an increase in date syrup fraction in tested samples led to a significant reduction in DPPH concentration, attributable to the free radical scavenging properties of date syrups. The hydrogen donation capacity of the tested samples was comparable to that of Vit. C, indicating that the syrups can function as hydrogen donors, thereby halting the radical chain reaction. Methanolic extracts of our date syrups had considerable antioxidant activity (figure 5.9). Using atmospheric open-pan heating at about 100°C, formation of water-soluble Maillard reaction products MRP, are recognized for their free radical scavenging properties (Yilmaz & Toledo, 2005). Nonetheless, significant variances are attributable to the evaporation method, with an IC_{50} of 505.81 ± 10.01 µg/mL of methanolic extract, observed at atmospheric pressure and elevated temperature (~110°C) much higher than 367.98 ± 17.6 µg/mL of methanolic extract for VAE (figure 5.9). This can be explained by the fact that low-temperature vacuum evaporation concentrates phenolic chemicals and other heat-sensitive antioxidants, decreasing thermal degradation. Our statements are contrast with those of Abbès et al (2013), using three date cultivars for producing date syrup. Results showed higher scavenging activity in concentrated date syrups obtained at atmospheric pressure at 100 °C, demonstrating lower IC_{50} values

(30.46 to 58.02 mg of date syrup/mL of distilled water) compared to those vacuum-evaporated at 60°C (33.80 to 70.17 mg of date syrup/mL of distilled water). Here we may suggest that increasing temperature improves the antioxidant activity of date syrups by better concentrating polyphenols. However, vacuum-evaporation at moderate temperature (60°C) can also influence polyphenol solubility and availability, but better protects heat-sensitive compounds as affirmed by Zhang & Xiao (2022). Also, antioxidant activity tested using DPPH is highly influenced by solvent used for diluting samples, as affirmed by Marinova & Batchvarov (2011).

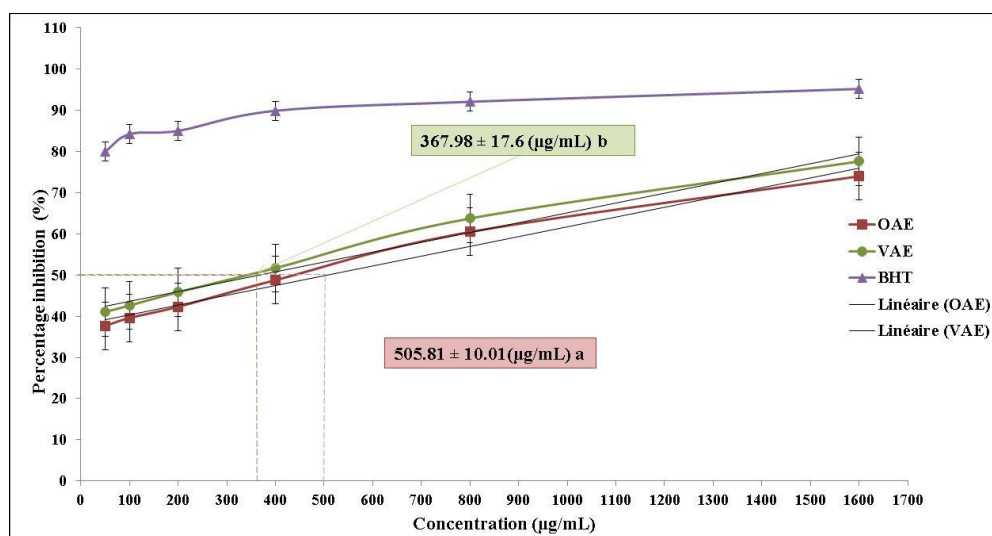


Figure 5.9. Free radical scavenging activities of the three DPAEs from the date pulp obtained by applying the optimum conditions of the three concentration methods: (OAE and VAE). BHT: butylated-hydroxytoluene as a standard antioxidant compound (positive control).

5.3. Conclusion

Vacuum-assisted concentration differs from the conventional method in that its moderate temperatures (~45°C) better preserve the bioactive and organoleptic properties of products, while limiting thermal alterations. Although both methods achieve ~70% TSS, VAE offers higher yields, controlled evaporation and reduced processing time, thanks to lower boiling temperatures and more efficient heat transfer. This technique represents a promising advance for the concentration of syrups and other heat-sensitive food matrices, such as tropical juices. Future research should further evaluate the sensory properties and stability of concentrated products to optimize their quality and durability during storage.

Our results and those of Abbès et al (2013) confirm that the antioxidant capacity of date syrups depends on temperature and the evaporation method. Furthermore, vacuum evaporation at low temperatures (45°C) reduces the thermal degradation of heat-sensitive

antioxidants, ensuring better antioxidant preservation, which is a valuable factor in optimizing the production of syrups rich in bioactive compounds.

The evaporation model of *Henderson and Pabis* could fit well into the kinetic behavior of concentrating date extract. The kinetic study carried out in this work was limited to a single experimental temperature, which did not allow an Arrhenius-type thermodynamic correlation to be established. In order to estimate the activation energy and better characterize the thermal sensitivity of the process, further tests at different temperatures will be required. Such an approach would pave the way for more comprehensive modeling and a deeper understanding of the mass transfer mechanisms involved.

*Conclusion and
perspectives*

General conclusion and perspectives

This thesis is part of a rigorous scientific approach aimed at adding value to a neglected local agricultural resource, the “*Mech Degla*” date variety, through the optimized production of high value-added natural syrup. This work has made it possible to overcome the traditional limitations associated with the use of dried dates, characterized by low commercial attractiveness due to their floury texture, by proposing an integrated protocol based on in-depth analysis of morpho-metric, physico-chemical and biochemical properties, followed by optimization of extraction and concentration processes.

Detailed characterization of the fruit highlighted its chemical profile rich in total sugars ($75.03 \pm 2.54\%$ FW), phenolic compounds (4.56 ± 0.09 mg GAE/g DW) and antioxidants (854.25 ± 31.07 $\mu\text{g/mL}$ of methanolic extract), confirming its potential as a functional raw material. Remarkably, the application of assisted extraction techniques, in particular microwave extraction (MAE), significantly improved extract yield and quality, while reducing time and energy consumption (4 min), paving the way for more sustainable and industrializable production.

Fine analysis by liquid chromatography coupled with tandem mass spectrometry (HPLC-MS/MS) identified a diverse array of 41 bioactive compounds present in the extract studied, including sugars, organic acids, nucleosides, carotenoids, proanthocyanidins, lignans, flavonols, flavones, saponins and sterol glycosides. This molecular richness testifies to the phytochemical complexity of plant material and justifies its major interest in the formulation of functional food products. The structural and functional diversity of these metabolites gives the extract significant antioxidant and therapeutic potential, likely to act on various biological mechanisms linked to the prevention of oxidative stress and the modulation of inflammatory responses.

These results underline the importance of integrating advanced analytical methods for exhaustive characterization of natural matrices, an essential prerequisite for any optimized industrial valorization. Indeed, precise knowledge of the chemical profile paves the way for standardization of extracts, a sine qua non for guaranteeing reproducibility and quality of

finished products. For future research, it seems essential to continue studying the *in vivo* bio-accessibility and bio-availability of these identified compounds, in order to gain a better understanding of their actual physiological efficacy.

The present study shows that the choice of aqueous extraction method for total soluble solids from date pulp must be guided by the specific beneficiation objective, as each process produces extracts with distinct characteristics influencing the quality and functionality of the final product. In particular, water bath extraction (WAE) yielded a significantly high sucrose concentration (139.12 ± 7.71 mg/mL aqueous date extract), positioning this extract as a potential source of refined sugars. On the other hand, unconventional techniques, namely microwave-assisted extraction (MAE) and ultrasonic-assisted extraction (UAE), generated extracts with no significant antibacterial activity, making them of particular interest for applications where the preservation of beneficial microbial flora is desired, notably in probiotic formulations and fermented products. This specificity could favour the integration of these extracts in functional food matrices aimed at boosting intestinal health without disturbing the natural microbial balance.

However, this lack of antimicrobial activity also suggests that these processes favor the selective extraction of bioactive compounds with antioxidant and nutritive properties rather than antimicrobial metabolites, thus paving the way for targeted exploitation according to the functional needs sought. The MAE method stood out for its higher extraction yield in aqueous extract ($79.9 \pm 1.54\%$), its high colorimetric intensity ($76.85 \pm 0.46 \times 10^{-3}$) and its higher concentration of total phenolic compounds (1.69 ± 0.04 mg GAE/mL aqueous date extract), reflecting a remarkable antioxidant capacity, confirmed by an IC_{50} value of 729.80 ± 12.87 μ g/mL methanolic extract. This efficiency, combined with an extraction time three times shorter than conventional methods, makes microwave irradiation a promising technique for the production of antioxidant-enriched syrups aimed at health-conscious consumers. For its part, ultrasonic extraction produced an extract rich in reducing sugars, notably glucose (50.86 ± 3.68 mg/mL aqueous date extract) and fructose (53.57 ± 4.16 mg/mL aqueous date extract), ensuring superior sweetness intensity and a balanced taste profile favorable to dietary formulations requiring high but controlled sweetness. Nevertheless, the limited ability of this method to extract all the solid matter highlights the need for further optimization of this process.

The comparative study of concentration methods demonstrated that vacuum evaporation (VAE), thanks to its moderate temperatures (~45°C), better preserves the bioactive and organoleptic properties of date syrup than open-heating evaporation (OAE). Despite similar total soluble solids contents (~74% TSS), OAE ensures more precise control, a relatively short processing time (60 min) and limits thermal degradation, thanks to lower vacuum boiling temperatures and more efficient heat transfer.

This technique represents a promising technological advance for the concentration of syrups and other heat-sensitive food matrices, such as tropical juices, making it possible to combine nutritional quality and industrial efficiency. In addition, the high sugar content (87.30±3.46% FW of date syrup) and enhanced antioxidant retention, confirmed by measurements of free radical scavenging activity ($IC^{50} = 367.98 \pm 17.6 \mu\text{g/mL}$ of methanolic extract), underline the importance of controlling thermal parameters to optimize the production of syrups that are both energetic and rich in bioactive compounds.

From a kinetic point of view, the Henderson and Pabis evaporation model proved suitable for describing the concentration behavior of date extract at the experimental temperature considered. However, the limitation to a single study temperature prevented the development of a complete thermodynamic model, in particular according to the Arrhenius model, essential for estimating the activation energy and characterizing the thermal sensitivity of the process.

Further experiments at different temperatures are essential to establish the key thermodynamic parameters, such as activation energy and rate constant, and thus to develop predictive modeling of concentration processes.

Following on from this study, several lines of research deserve to be explored in order to strengthen the technological mastery and industrial valorization of concentrated date syrups:

- ✓ In-depth evaluation of the sensory properties and physico-chemical and microbiological stability of syrups concentrated by VAE over extended storage periods, in order to guarantee their organoleptic, nutritional and hygienic quality, right up to their use-by date.
- ✓ Investigation of the combined effects of vacuum concentration with other emerging technologies, such as membrane evaporation or freeze-drying, to design innovative hybrid processes combining energy efficiency and optimal preservation of bioactives.

- ✓ Pilot-scale studies and techno-economic analyses to validate industrial feasibility and optimize costs, thus promoting the large-scale adoption of VAE in the date syrup industry.

These orientations will consolidate the place of date syrups concentrated by vacuum evaporation in sustainable agri-food circuits, meeting the sector's growing demands for quality and innovation.

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Annexes

Annexes

Annex 1. Calibration curves

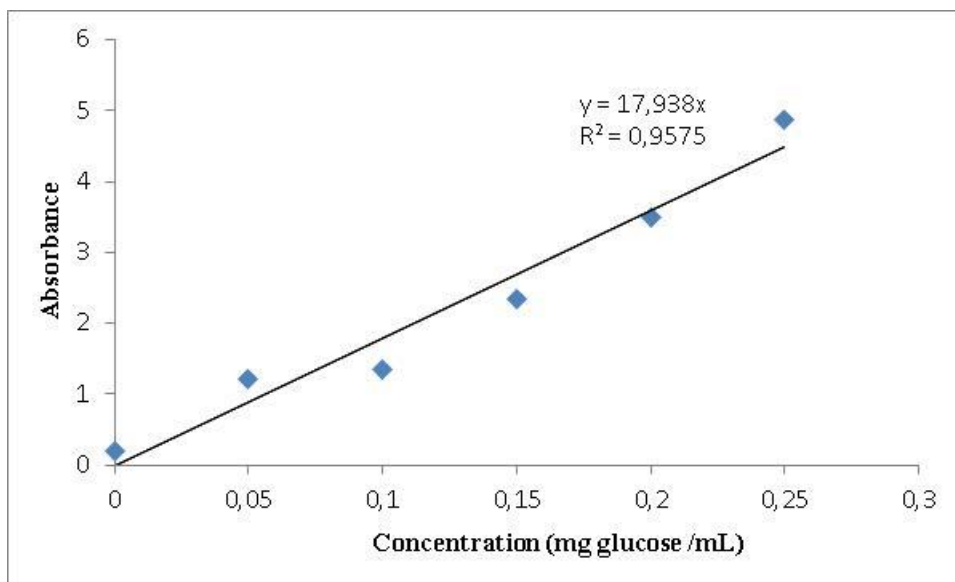


Figure 1. Glucose calibration curve

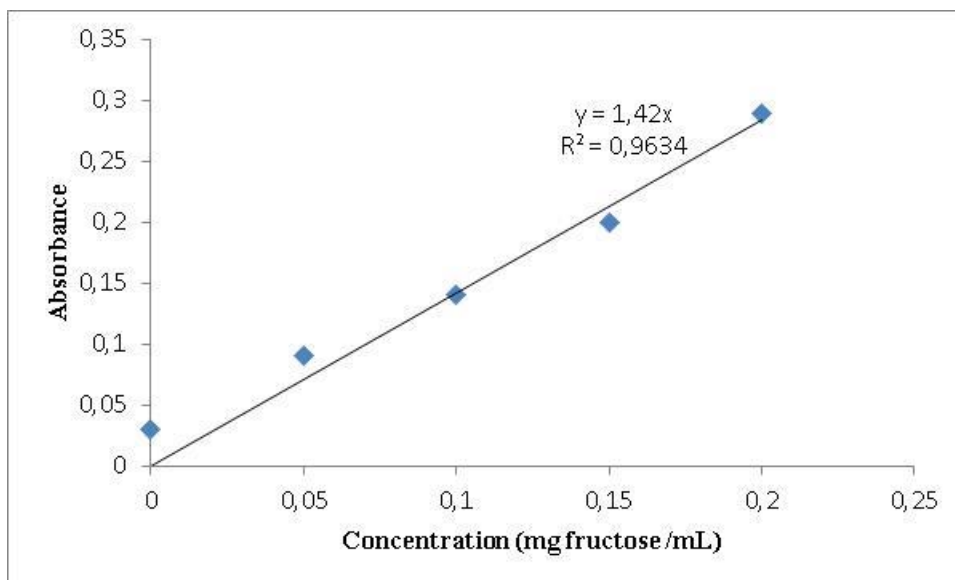


Figure 2. Fructose calibration curve

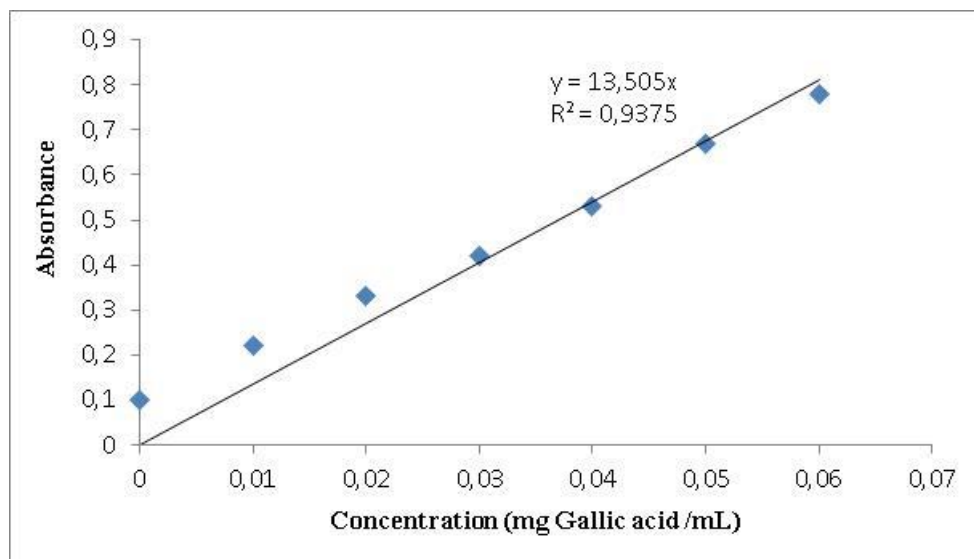


Figure 3. Gallic acid calibration curve.

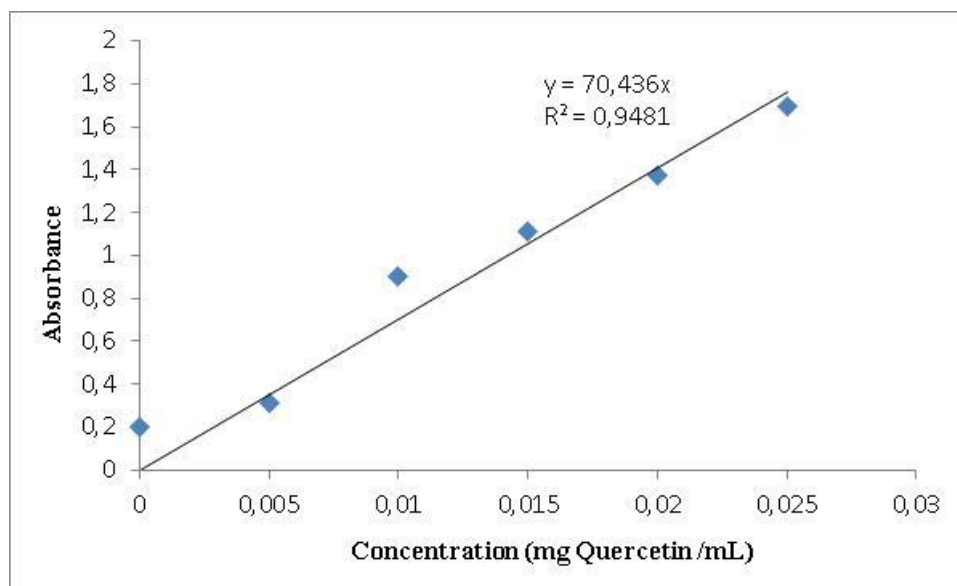


Figure 4. Quercetin calibration curve

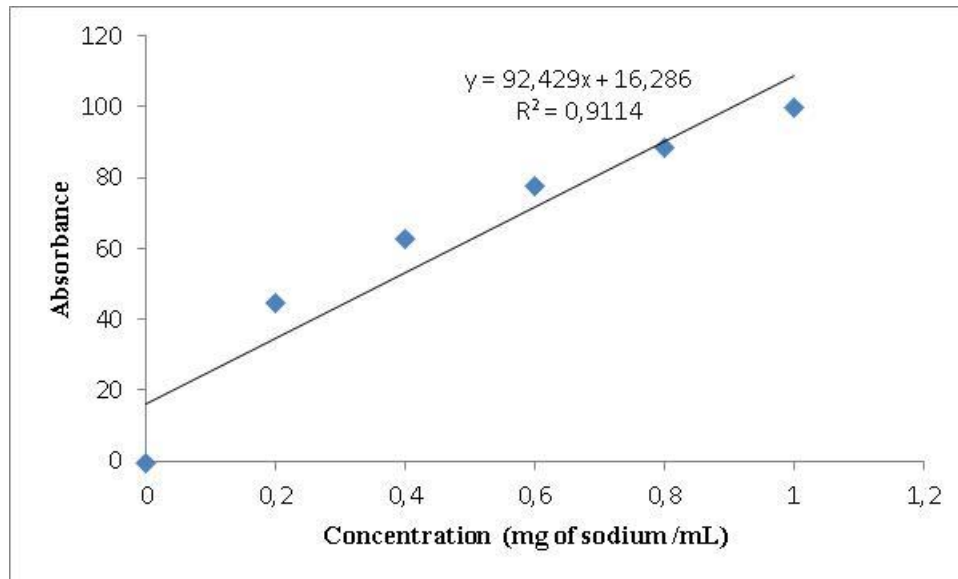


Figure 5. Sodium calibration curve

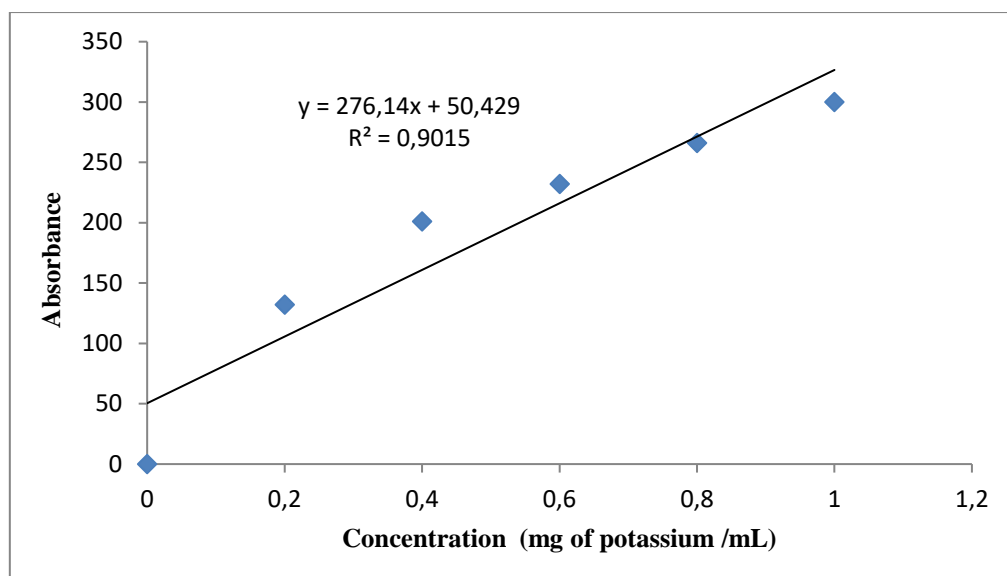


Figure 6. Potassium calibration curve

Summary

This thesis deals with the valorization of the Algerian dry date of the low market value variety “*Mech Degla*”, through the optimization of the production of high value-added natural syrup. The work is part of a sustainable agri-food processing approach, mobilizing modern extraction and concentration methods. The study began with the physico-chemical and biochemical characterization of the pulp, revealing a richness in total sugars (75.03 ± 2.54 % FW), phenolic compounds (4.56 ± 0.09 mg GAE/g DW) and a notable antioxidant activity (854.25 ± 31.07 $\mu\text{g/mL}$). Microwave-assisted extraction (MAE) significantly improved extract yield and quality, while reducing time (4 min) and energy consumption. LC-MS/MS analysis identified 44 different bioactive compounds, including flavonoids, saponins and organic acids. Aqueous extracts obtained by MAE showed a high aqueous extract yield (79.9 ± 1.54 %), with and high colorimetric intensity ($76.85 \pm 0.46 \times 10^{-3}$), while water bath extraction (WAE) yielded a significantly high sucrose concentration (139.12 ± 7.71 mg/mL aqueous date extract). Ultrasonic extraction (UAE) produced an extract rich in reducing sugars, notably glucose (50.86 ± 3.68 mg/mL aqueous date extract) and fructose (53.57 ± 4.16 mg/mL aqueous date extract). Processing into syrup was optimized by vacuum evaporation (VAE), which showed improved retention of antioxidants ($\text{IC}_{50} = 367.98 \pm 17.6$ $\mu\text{g/mL}$) and total soluble solids (~74% TSS), including sugar richness (87.30 ± 3.46 % FW of date syrup). The kinetic model of “*Henderson and Pabis*” was used to model concentration. Prospects include the study of long-term stability, full thermodynamic modeling and the integration of hybrid technologies. This research proposes a sustainable valorization route for a local resource, meeting the requirements of the functional agri-food sector.

Key-words: date-fruit, syrup, optimization, extraction, concentration, quality.

Résumé

Cette thèse porte sur la valorisation de la datte sèche algérienne de variété de faible valeur marchande «*Mech-Degla*», à travers l'optimisation de la production d'un sirop naturel à haute valeur ajoutée. Le travail s'inscrit dans une démarche de transformation agroalimentaire durable, mobilisant des méthodes modernes d'extraction et de concentration. L'étude débute par la caractérisation physico-chimique et biochimique de la pulpe, révélant une richesse en sucres totaux (75.03 ± 2.54 % FW), composés phénoliques (4.56 ± 0.09 mg GAE/g DW) et une activité antioxydante notable (854.25 ± 31.07 $\mu\text{g/mL}$). L'extraction assistée par micro-ondes (MAE) a permis d'améliorer significativement le rendement et la qualité des extraits tout en réduisant le temps (4 min) et la consommation énergétique. L'analyse LC-MS/MS a permis d'identifier 44 composés bioactifs variés, notamment des flavonoïdes, saponines et acides organiques. Les extraits aqueux obtenus par MAE présentaient un rendement en extrait aqueux élevé (79.9 ± 1.54 %), avec et une forte intensité colorimétrique ($76.85 \pm 0.46 \times 10^{-3}$), tandis que l'extraction par bain marie (WAE) a permis d'obtenir une concentration significativement élevée en saccharose (139.12 ± 7.71 mg/mL d'extrait aqueux de datte). De son côté, l'extraction par ultrasons (UAE) a produit un extrait riche en sucres réducteurs, notamment en glucose (50.86 ± 3.68 mg/mL d'extrait aqueux de datte) et fructose (53.57 ± 4.16 mg/mL d'extrait aqueux de datte). La transformation en sirop a été optimisée par l'évaporation sous vide (VAE), qui a montré une meilleure conservation des antioxydants ($\text{IC}_{50} = 367.98 \pm 17.6$ $\mu\text{g/mL}$) et des solides solubles totaux (~74 % TSS), dont la richesse en sucres (87.30 ± 3.46 % FW de sirop de datte). Le modèle cinétique de «*Henderson et Pabis*» a été utilisé pour modéliser la concentration. Les perspectives incluent l'étude de la stabilité à long terme, la modélisation thermodynamique complète et l'intégration de technologies hybrides. Cette recherche propose une voie de valorisation durable pour une ressource locale, répondant aux exigences du secteur agroalimentaire fonctionnel.

Mots clé : fruit, datte, sirop, optimisation, extraction, concentration, qualité.

ملخص

تركز هذه الأطروحة على تطوير التمور الجافة الجزائرية من الصنف منخفض القيمة السوقية “ماش دقلة”، من خلال تحسين إنتاج شراب طبيعي عالي القيمة المضافة. ويندرج هذا العمل في إطار نهج المعالجة الزراعية الغذائية المستدامة، باستخدام طرق الاستخلاص والتركيز الحديثة. وقد بدأت الدراسة بالتوصيف الفيزيائي والكيميائي والحيوي لللب، وكشفت عن مستوى عالٍ من السكريات الكلية (75.03 ± 2.54 % من الوزن الزائد)، والمركبات الفينولية (4.56 ± 0.09 ملغم من السكر الإجمالي/غرام من وزن الجسم/غ من الماء الثقيل) ونشاط كبير مضاد للأكسدة (854.25 ± 31.07 ميكروغرام/ملليتر). حسن الاستخلاص بمساعدة الميكروويف (MAE) بشكل كبير من محصول وجودة المستخلصات مع تقليل الوقت (4 دقائق) واستهلاك الطاقة. حدد تحليل LC-MS/MS 44 مركبًا نشطًا بيولوجيًا مختلفًا، بما في ذلك مركبات الفلافونويد والصابونين والأحماض العضوية. أظهرت المستخلصات المائية التي تم الحصول عليها عن طريق الاستخلاص المائي (MAE) إنتاجية عالية من المستخلص المائي (79.9 ± 1.54 %)، مع كثافة لونية عالية ($76.85 \pm 0.46 \times 10^{-3}$)، بينما أدى الاستخلاص بالحمام المائي (WAE) إلى تركيز عالٍ من السكروز بشكل ملحوظ (139.12 ± 7.71 ملغم/ملليتر من مستخلص التمر المائي). وأنتج الاستخلاص بالموجات فوق الصوتية (UAE) مستخلصًا غنيًا بالسكريات المختزلة، وخاصة الجلوكوز (50.86 ± 3.68 ملغم/ملليتر من مستخلص التمر المائي) والفركتوز (53.57 ± 4.16 ملغم/ملليتر من مستخلص التمر المائي). تم تحسين التحويل إلى شراب عن طريق التبخير بالتفريغ (VAE)، والذي أظهر حفظًا أفضل لمضادات الأكسدة (367.98 ± 17.6 IC_{50} ميكروغرام/مل) والمواد الصلبة الكلية القابلة للذوبان (حوالي 74% من المواد الصلبة القابلة للذوبان)، بما في ذلك ثراء السكر (87.30 ± 3.46 % من شراب التمر). تم استخدام النموذج الحركي “هندرسون وبابيس” لنمذجة التركيز. تشمل الآفاق دراسة الاستقرار على المدى الطويل، والنمذجة الديناميكية الحرارية الكاملة ودمج التقنيات الهجينة. يقدم هذا البحث طريقة مستدامة لإضافة قيمة مضافة إلى مورد محلي، وتلبية متطلبات قطاع الأغذية الزراعية الوظيفي.

الكلمات المفتاحية: التمور، الشراب، التحسين، الاستخلاص، التركيز، الجودة.