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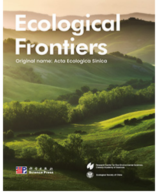

Full length article

Optimization of total phenolic extraction from three Moroccan date palm cultivars (*Phoenix dactylifer* L.) using mixture design and triangular surfaces

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ABSTRACT

This study aimed to optimize total phenolic content (TPC) extraction from dates using solvent mixtures, simplex-centroid design, and desirability analysis. After identifying the most efficient solvents (water, methanol, and ethanol) using the Folin-Ciocalteu method, fixed combinations and cubic models were used to determine the optimum proportions for each cultivar. The simplex centroid design matrix showed that for the Mejhoul cultivar, a mixture of 1/6 water, 1/6 methanol, and 2/3 ethanol yielded a maximum TPC value of 133.97 mg GAE/100 g dry weight. For the Bousthammi cultivar, the optimum blend was 2/3 water, 1/6 methanol, and 1/6 ethanol, achieving a maximum extraction of 192.83 mg GAE/100 g dry weight. For the Boufeggous cultivar, the use of alone ethanol (1/1) produced the highest CPT value, with 301.33 mg GAE/100 a dry weight. The desirability analysis confirmed these results while identifying other optimal combinations. For Mejhoul, the binary interaction between 20 % water and 80 % ethanol resulted in the maximum yield. For Boufeggous, a ternary mixture of 50 % water, 25 % methanol, and 25 % ethanol produced the best results, whereas, for Bousthammi, the ideal mixture was comprised of 75 % water, 12.5 % methanol, and 12.5 % ethanol. These results highlight the effectiveness of this method and its adaptability to the biochemical specificities of each date cultivar, offering a robust technique for maximizing TPC extraction and adding value to Moroccan dates.

1. Introduction

Date palm (*Phoenix dactylifera* L.) occupies an essential place in Moroccan agriculture, with a cultivated area of approximately 71,369 ha. Over the past two decades, national date production has risen considerably from 32,400 tons in 2001 to 125,329 tons in 2016 [1], which reached approximately 143,163 tons [2]. The average annual date consumption in Morocco is estimated at 2.82 kg per capita [1]. The country has several cultivars (contraction of cultivated variety) that designate plant varieties selected and maintained by cultivation for their specific characteristics, such as flavor, biochemical composition of the fruit, and nutritional qualities.

Dates are a major source of carbohydrates, notably simple sugars, such as glucose, fructose [3,4], and sucrose [5]. They are also rich in dietary fiber, essential minerals (iron, potassium, selenium, calcium), and vitamins (C, B1, B2, A, riboflavin, and niacin), although their fat and protein contents are relatively low [6]. Their high energy value (307–354 kcal/100 g) and low water content (13–25 %, decreasing with ripening) make them particularly nutritious fruits [7].

In addition to their nutritional value, dates are an important source of bioactive compounds, notably secondary metabolites, with remarkable antioxidant properties. These compounds, such as anthocyanins, flavonoids, carotenoids, sterols, and procyanidins, are recognized for their beneficial health effects, including antimutagenic, antimicrobial, anti-inflammatory, gastroprotective, hepatoprotective, nephroprotective, anticancer, and immunostimulatory properties[7, 8]. Polyphenols, particularly phenolic acids, and flavonoids, are major secondary metabolites abundant in dates, which are distinguished by their diversity and high concentration compared to other fruits [9]. However, their composition varies according to several factors, such as cultivar, ripening stage, environmental and agronomic conditions, and growing area [10]. Phytochemical studies have shown that date pulp contains a significant concentration of phenolic acids, including para-coumaric, gallic, protocatechic, tyrosol, vanillic, and syringic acids. Gallic acid is

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generally the dominant compound, with concentrations varying between 1.35 and 1.53 g/kg of sample [11].

To our knowledge, no previous studies have been carried out in Morocco to optimize date polyphenol extraction using an approach based on solvent mixture modeling. The extraction efficiency of phenolic compounds is highly dependent on the nature of the solvent and its polarity as well as on the interactions between solvents when combined. Thus, identifying the optimum solvent combination would not only improve polyphenol yields but also enhance the value of local resources and contribute to the development of new food and nutraceutical products based on Moroccan dates. In this context, this study aimed to optimize the extraction of total phenolic compounds from the pulp of three Moroccan date cultivars (Boufegouss, Bousthammi, and Mejhoul) harvested from different regions. To this end, we used an approach based on a simplex-centroid mixing scheme and triangular surfaces to identify the most efficient solvent combination (water, acetone, acetonitrile, ethanol, and methanol) for maximizing polyphenol extraction.

2. Material and methods

2.1. Plant material

Date palm cultivars (*Phoenix dactilyfera* L.) "Mejhoul," "Bousthammi," and "Boufeggous" are harvested in the Tamar stage in different regions of Morocco. Table 1 provides details of the selected cultivars and sampling locations. Trees were randomly selected. Samples returned to the laboratory were freeze-dried, pulverized, and stored at −20 °C for subsequent extraction and analysis.

2.2. Total phenolic content (TPC)

Polyphenol was extracted as described by Chansriniyom et al. [12]. Briefly, 50 mg of the arterial fraction of ST was sonicated in 1 mL of the selected solvent for 20 min. The mixture was then centrifuged at 6000 rpm for 15 min, and the supernatant obtained was stored at 4 °C. The total phenolic content (TPC) was determined spectrophotometrically using a colorimetric technique modified from the Folin-Ciocalteu reagent [13]. Mix 450 μl of diluted Folin-Ciocalteu reagent solution with 50 μl of extract or standard gallic acid solution. After incubation for 5 min at room temperature (26 °C) in a vortex mixer (VELEP SCIENTIFICA), 450 μl Na_2CO_3 solution (75 $g \cdot L^{-1}$) was added, and the mixture was shaken again. After 2 h of incubation at room temperature, the absorbance was measured at 760 nm using a UV/visible light spectrophotometer (RAYLEIGH). The total polyphenol content was determined using a calibration curve and expressed in mg GAE.100 g^{-1} DW or gallic acid equivalents per 100 g [14].

2.3. Mixture design

The simplex centroid method using TIBCO Software Statistica 13.3.0, Palo Alto, California, United States of America (USA), was used to study the effects of different solvents on the extraction of phenolic compounds from date fruits and to determine the optimal solvent mixture to maximize the phenolic content. For the simplex centroid design, triangles were used to score different solvents, with the alone component at the top representing 100 % of each solvent. Each solvent in the system was inspected at six levels, based on the 12 tests shown in Fig. 1. Linear (Eq. (1)) and quadratic (Eq. (2)) and special cubic (Eq. (3)), mathematical models were evaluated.

$$\text{Linear} : yn(x) = \Sigma qi = 1\beta ixi \tag{1}$$

$$\text{Quadratic} : \mathrm{yn(x)} = \Sigma \mathrm{qi} = 1\beta \mathrm{ixi} + \mathrm{q}\Sigma 1\mathrm{i} < \mathrm{j}\Sigma \beta ijxixj \tag{2}$$

$$\begin{aligned} &\text{Special cubic} : \mathrm{yn(x)} \\ &\quad = \Sigma \mathrm{q}\ i = 1\ \beta \mathrm{ixi} + \mathrm{q}\Sigma 1\ \mathrm{i} \\ &\quad < \mathrm{j}\Sigma \mathrm{q}\ \mathrm{j}\ \beta \mathrm{ijxixj} + \mathrm{q}\Sigma 2\ \mathrm{i} < \mathrm{j}\ \mathrm{q}\Sigma 1\ \mathrm{j} \\ &\quad < \mathrm{k}\Sigma \mathrm{q}\ \mathrm{k}\ \beta \mathrm{ijkxixjxk} \end{aligned} \tag{3}$$

yn denotes the anticipated response function, which has been extensively examined in the context of total phenols. The independent variables xi, xj, and xk are associated with the constituents utilized in the blending scheme, namely, water, methanol, and ethanol, where xijk falls within the range of 0 to 1. The parameters βi, βij, and βijk denote the linear coefficient about the individual component i, the quadratic binary interaction coefficient for components i and j, and the cubic ternary interaction coefficient for components i, j, and k.

2.4. Statistical analysis

Analysis of variance (ANOVA) and regression analysis were used to assess mathematical predictive models ($p < 0.05$). Duncan's mean comparison test ($p \leq 0.05$) was employed to assess the differences between different solvents for TPC extraction using SPSS statistics 21. The development of the surface was achieved using the adjusted modules. Employing the desirability function proposed by Derringer and Suich [15] to maximize the outcomes of all variables. The mathematical models were validated by implementing three supplementary tests under improved conditions, as determined by the desirability function. A student's *t*-test was used to evaluate experimental values against estimated responses falling within a 95 % confidence interval.

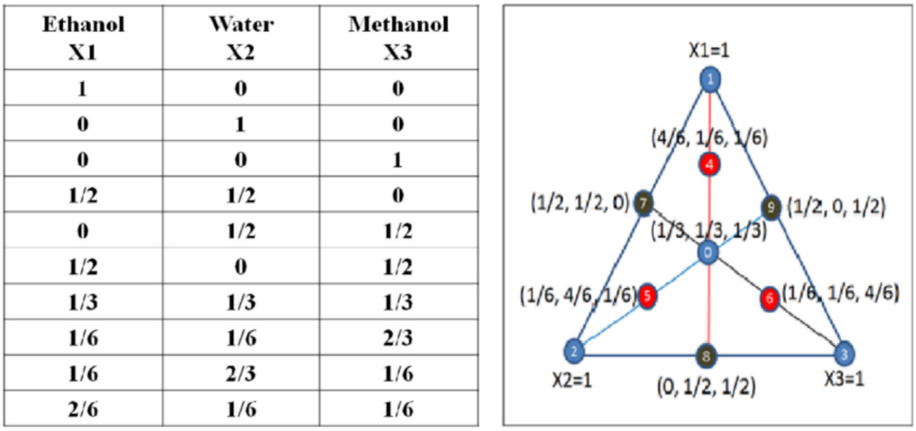
3. Results

3.1. Selection of optimal solvents

Figure 2 shows the total polyphenol content of three date palm cultivars (Boufegouss, Bousthammi, and Mejhoul) as a function of different extraction solvents (water, methanol, ethanol, acetone, and acetonitrile). The results showed that polyphenol extraction efficiency varied significantly according to the solvent used. For the Boufegouss cultivar, ethanol, water, and methanol proved to be the most efficient solvents (no significant difference at pin less than 0.05), with polyphenol contents of 301.33, 278.03 and 257.23 mg GAE /100 g dry weight. At the same time, acetonitrile showed much less efficient extraction, with only 76.43 mg GAE /100 g dry weight. For the Bousthammi cultivar, the most efficient solvents were water and methanol, each extracting around 104 mg GAE/100 g dry weight, whereas acetonitrile produced the lowest amount of polyphenols (43 mg GAE/100 g dry weight). For the Mejhoul cultivar, methanol gave the best results at 115.57 mg/g, followed by ethanol (89.39 mg SAG /100 g dry weight) and water (87.03 mg SAG /100 g dry weight), while acetonitrile also performed the least well (54.9 mg SAG /100 g dry weight). There was also some variability between the varieties. The Boufegouss cultivar showed higher overall polyphenol content, particularly with aqueous solvents

Table 1
Sampling symbols and climatic characterization of different geographical locations of varieties.

Varieties	Region	Altitude (m)	Latitude	Longitude	Minimum temperature (°C)	Maximum temperature (°C)	Rainfall (mm)
Mejhoul	Rissani	759	31°17′18.8556″N	4°16′30.9174″W	5	36.34	15.66
Bousthammi	Zagora	724	30°19″50′ N	5°50″17′W	6.92	42.19	16.33
Boufeggous	Tata	688	29°44′,784 N	7°58′,176 W	6	40	12



Ethanol X1	Water X2	Methanol X3
1	0	0
0	1	0
0	0	1
1/2	1/2	0
0	1/2	1/2
1/2	0	1/2
1/3	1/3	1/3
1/6	1/6	2/3
1/6	2/3	1/6
2/6	1/6	1/6

Fig. 1. Illustration representing the mixture design simplex axial design (SAD). X1 = Ethanol, X2 = H_2O, X3 = Méthanol.

(water and methanol), than the other cultivars. Conversely, the Bousthammi cultivar exhibited the lowest values under most extraction conditions, particularly with acetone and acetonitrile. The Mejhoul cultivar was in an intermediate position, with optimal results with methanol; however, polyphenol levels were generally lower than those of the Boufegouss cultivar.

3.2. Solvent mixture composition in TPC extraction

The results obtained for TPC extracted from date fruits using different solvents range from 41.67 to 324.67 mg GAE.100 g^{-1} DW (Table 2), the polyphenol content of the different extracts, and their mixtures. For the Mejhoul cultivar, the best TPC was 133.97 mg GAE.100 g DW using a mixture of solvents containing water, methanol, and ethanol in percentages of 1/6, 1/6, and 2/3, respectively. For the Bousthammi cultivar, the polyphenol-rich extract contains 192.83 GAE.100 g DW, with a solvent mixture of 2/3 water, 1/6 methanol, and 1/6 ethanol. Finally, the Boufegouss cultivar, with its isolated ethanol, gives the highest yield of TPC with a content of 324.67 GAE.100 g DW.

3.3. Analysis of variance (ANOVA)

Table 3 presents an examination of variance (ANOVA). Transitioning from a linear to a quadratic and specialized cubic model enhanced the fitness of the regression analysis. The significance level, denoted as p, indicates a substantial distinction among the averages when $p < 0.05$, and the lack of a significant distinction when p 0.10 [16]. Notably, the specialized cubic model proves to be dependable, precise, and the most appropriate (p-value <0.05) for forecasting the behavior of the mixtures [17]. The correlation coefficients were R-sqr = 0.994 and R-adjusted = 0.992. Polynomial equations that delineate the correlation between the acquired responses are as follows:

$$
\begin{aligned}
\mathrm{TPC(Bousthammi)} = {} & +0.954^{*}\mathrm{ethanol} + 0.406^{*}\mathrm{water} + 0.554^{*}\mathrm{methanol} \\
& + 0.696^{*}\mathrm{erhanol}^{*}\mathrm{water} + 0.277^{*}\mathrm{ethanol}^{*}\mathrm{methanol} \\
& + 0.971^{*}\mathrm{water}^{*}\mathrm{methanol} \\
& + 17.373^{*}\mathrm{ethanol}^{*}\mathrm{water}^{*}\mathrm{methanol} \\
& + 5.950^{*}\mathrm{ethanol}^{*}\mathrm{water}^{*}(\mathrm{ethanol} - \mathrm{water}) \\
& + 7.286^{*}\mathrm{ethanol}^{*}\mathrm{methanol}^{*}(\mathrm{ethanol} - \mathrm{methanol}) \\
& + 0,
\end{aligned}
$$

$$
\mathrm{TPC(Boufeggous)} = \begin{aligned}
& 0.622^{*}\ \mathrm{ethanol} + 0.542^{*}\ \mathrm{water} + 0.632^{*}\ \mathrm{methanol} \\
& + 0.480^{*}\ \mathrm{ethanol}^{*}\ \mathrm{water} + 0.878^{*}\ \mathrm{ethanol}^{*} \\
& \mathrm{methanol}–0.1676^{*}\ \mathrm{water}^{*}\ \mathrm{methanol} \\
& + 77.479^{*}\ \mathrm{ethanol}^{*}\ \mathrm{water}^{*}\ \mathrm{methanol}–8.2433^{*}\ \mathrm{ethanol}^{*} \\
& \mathrm{water}^{*}(\mathrm{ethanol} - \mathrm{water}) \\
& + 20.676^{*}\ \mathrm{ethanol}^{*}\ \mathrm{methanol}^{*}(\mathrm{ethanol} - \mathrm{methanol}) + 0,
\end{aligned}
$$

$$
\mathrm{TPC(Mejhoul)} = \begin{aligned}
& +0.870^{*}\mathrm{ethanol} + 0.813^{*}\mathrm{water} + 0.923^{*}\mathrm{methanol} \\
& + 0.3672^{*}\mathrm{ethanol}^{*}\mathrm{water} - 0.222^{*}\mathrm{ethanol}^{*}\mathrm{methanol} \\
& - 0.281^{*}\mathrm{water}^{*}\mathrm{methanol} + 4.493^{*}\mathrm{ethanol}^{*}\mathrm{water}^{*}\mathrm{methanol} \\
& + 1.759^{*}\ \mathrm{ethanol}^{*}\mathrm{water}^{*}(\mathrm{ethanol} - \mathrm{water}) \\
& - 2.866^{*}\mathrm{ethanol}^{*}\mathrm{methanol}^{*}(\mathrm{ethanol} - \mathrm{methanol}) + 0.
\end{aligned}
$$

3.4. Contour plots analysis

The contour diagram represents a triangle with each corner indicating the percentage of each extraction solvent (ethanol, methanol, and water). Each point inside the triangle corresponds to a specific combination of these solvents, and the colors indicate the concentration of the total polyphenols in the extract. The red areas represent high polyphenol concentrations, whereas the green areas correspond to lower values. The color transition from green to red indicates the influence of different solvent combinations on polyphenol content. In the case of the Majhoul cultivar, the presence of red zones in the upper region of the triangle suggests that the maximum polyphenol concentrations were reached for high proportions of ethanol (close to 1.00), with little or no methanol and water. Conversely, higher proportions of methanol or water appeared to decrease the polyphenol content. Meanwhile, the 3D response surface shows the same information from a three-dimensional perspective, facilitating visualization of the response's maximum and minimum points. The vertical axis represents the concentration of total polyphenols, whereas the other two axes show the proportions of methanol and ethanol. The colored surface illustrates the variation in polyphenols as a function of the solvent, with color codes identical to those of the contour plot. This representation also shows that the polyphenol content is the highest when a high proportion of ethanol is used, without methanol or water, as shown by the red part of the surface. In contrast, combinations with more methanol or water resulted in lower values (green and yellow areas) (Fig. 3A). For the Boufgouss cultivar, the concentration of total polyphenol peaks (dark red areas) when the mixture contained methanol, ethanol, and water. In contrast, a higher concentration of ethanol appears to significantly reduce polyphenol content, as shown by the green region in the left-hand corner of the triangle. The 3D view also shows that the optimum response is achieved through a positive interaction between water, methanol, and ethanol, while a high proportion of ethanol appears to reduce the extraction efficiency, leading to lower polyphenol concentrations (Fig. 3B). For the Bousthammi cultivar, the central peak of this surface confirms the optimal proportions identified in the contour plot with high proportions of water and little methanol and ethanol, where the TPC reaches its maximum. This surface also showed a decrease in TPC when the proportion of any of the solvents exceeded the optimal values, indicating that excess methanol, ethanol, or even water reduced the efficiency of polyphenol extraction. The 3D surface exhibited a decrease in the TPC when the proportion of one solvent exceeded the optimum

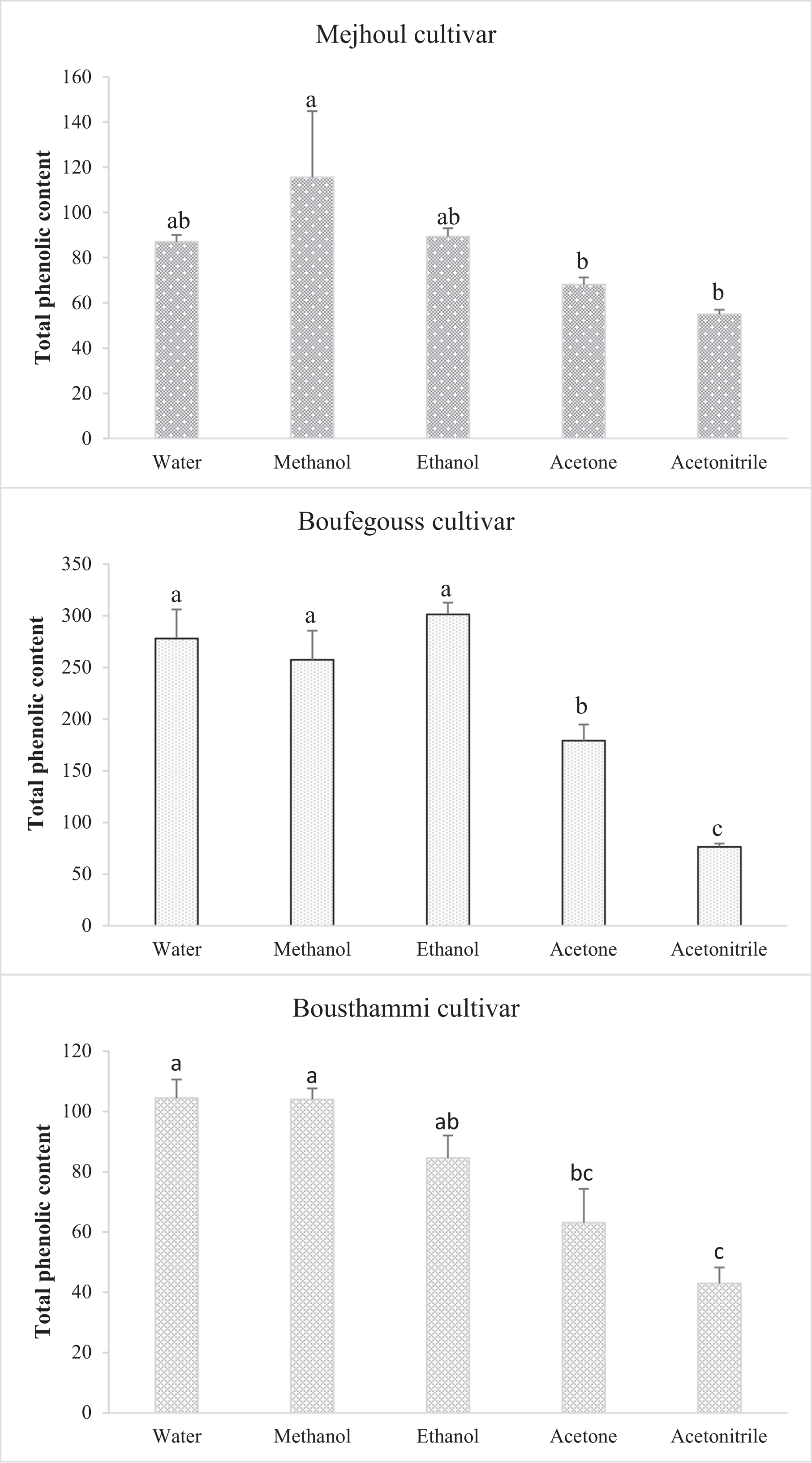


Fig. 2. Effect of different solvents on total phenolic content (TPC). For each cultivar of date palm, the TPC having the same letter are not different according to Duncan's test ($p \leq 0.05$).

value. This means that an excess of one solvent, at the expense of the other solvents, reduces the efficiency of polyphenol extraction. For example, excessive methanol and ethanol led to a drop in TPC (dark red areas) (Fig. 3C).

The graphs in Fig. 4 show the desirability as a function of the three solvents (water, methanol, and ethanol) for optimizing the extraction of total polyphenols (TPC) from the varieties studied. For the Majhoul cultivar, in the upper line of the graphs representing TPC, it was observed that for

Table 2
Matrix of conception axial simplex and phenolic content of the different solvent mixture's extracts.

				TPC mg GAE /100 g dry weight		
	Water	Methanol	Ethanol	Mejhoul cultivar	Boufegouss cultivar	Bousthammi cultivar
1	1/1	0	0	87.03 ± 0.05	278.03 ± 0.29	104.43 ± 0.11
2	0	1/1	0	115.56 ± 0.08	257.23 ± 0.23	104 ± 0.06
3	0	0	1/1	89.33 ± 0.08	**301.33 ± 0.30**	84.57 ± 0.13
4	1/2	1/2	0	85.17 ± 0.06	118.8 ± 0.06	87.47 ± 0.13
5	0	1/2	1/2	71.576 ± 0.08	41.67 ± 0.03	74.33 ± 0.11
6	1/2	0	1/2	75.9 ± 0.09	71.83 ± 0.13	84.4 ± 0.14
7	1/3	1/3	1/3	65 ± 0.04	74.03 ± 0.08	158.87 ± 0.08
8	1/6	1/6	2/3	**133.97 ± 0.02**	47.3 ± 0.08	61.1 ± 0.16
9	1/6	2/3	1/6	107.7 ± 0.07	45.8 ± 0.04	64.6 ± 0.03
10	2/3	1/6	1/6	114.69 ± 0.11	59.83 ± 0.09	**192.83 ± 0.03**

Table 3
The ANOVA results of regression models from simplex centroid design.

		SS Effect	Df Effect	MS Effect	F-value	P-value	R-Sqr	R2-Adj
TPC Mejhoul	Linear	0.0199	2.0000	0.0100	0.3367	0.7171	0.0243	0.0000
	Quadratic	0.1304	3.0000	0.0435	1.5600	0.2250	0.1835	0.0134
	Special Cubic	0.1622	1.0000	0.1622	7.3656	0.0124	0.3816	0.2203
	Cubic	0.0597	2.0000	0.0299	1.4034	0.2679	0.4545	0.4669
	Total Adjusted	0.8192	29.0000	0.0283				
TPC Bousthammi	Linear	1.8764	2.0000	0.9382	5.2335	0.0120	0.2794	0.2260
	Quadratic	1.3497	3.0000	0.4499	3.0933	0.0460	0.4803	0.3720
	Special Cubic	0.8798	1.0000	0.8798	7.7507	0.0106	0.6113	0.5099
	Cubic	1.9980	2.0000	0.9990	34.2350	0.0000	0.9088	0.8740
	Total Adjusted	6.7167	29.0000	0.2316				
TPC Boufegouss	Linear	1.0391	2.0000	0.5195	0.3457	0.7108	0.0247	0.0000
	Quadratic	12.2960	3.0000	4.0987	3.4781	0.0316	0.3204	0.1788
	Special Cubic	17.4987	1.0000	17.4987	37.3224	0.0000	0.7409	0.6733
	Cubic	4.9248	2.0000	2.4624	8.8260	0.0917	0.8592	0.8056
	Total Adjusted	41.6173	29.0000	1.4351				

SS: sum of squares, Df: degree of freedom, MS: mean of square, R-Sqr: coefficient of determination, R-adj: coefficient of determination adjusted.

water, TPC increased slightly at low concentrations (approximately 20 %) and then decreased as the proportion of water increased, suggesting that high water concentrations do not favor optimal extraction. For methanol, the TPC peaked at an intermediate concentration and then gradually decreased with higher concentrations, indicating an optimal effect of methanol at low concentrations. For ethanol, on the other hand, TPC peaks at high concentrations, confirming its effectiveness in extracting large quantities of polyphenols. The lower line, representing desirability, shows that desirability is low for water, indicating that it is less effective at the proportions tested. For methanol, desirability also decreased at high concentrations, confirming that it is not optimal for maximizing TPC. In contrast, for ethanol, the desirability peaks at approximately 80 %, indicating that it is the most favorable solvent for polyphenol extraction under the conditions studied. Finally, the overall desirability graph on the right shows an ascending line, confirming that the maximum experimental conditions for TPC were reached with a high proportion of ethanol (approximately 80 %). This confirmed that ethanol was the most efficient solvent for this date cultivar, while high proportions of water and methanol reduced the extraction efficiency (Fig. 4A). For Boufegouss, the individual desirability plots for each solvent showed that the CPT curve peaked at approximately 3.5746 mg WAS/100 g at a concentration of 50 % water, confirming that this proportion is optimal for polyphenol extraction. Furthermore, the maximum polyphenol content was observed with 25 % methanol, indicating that this concentration was ideal for the blend. Similarly, 25 % ethanol yielded the best TPC results. In each case, when the concentration of each solvent was too low or too high, the polyphenol content decreased, suggesting that a precise balance was required to achieve high TPC. The combined desirability graph reveals an optimized polyphenol content (TPC) of approximately 3.5080 mg GAE/100 g, with a desirability value of 1. This optimization corresponds to the ideal solvent proportions of 50 % water, 25 % methanol, and 25 % ethanol. The importance of balance is underlined by the linear relationship between desirability and TPC, indicating that, to maximize TPC, it is necessary to maintain a precise balance between solvents, thus confirming the proportions identified (Fig. 4B). Individual desirability plots for each solvent for the Bousthammi cultivar revealed that TPC peaked at approximately 75 % water, indicating that this proportion is optimal for polyphenol extraction. For methanol, the ideal concentration was approximately 12.5 %, which corresponded to the maximum TPC observed for this solvent in the blend. Similarly, for ethanol, an optimum concentration of 12.5 % is necessary to achieve high TPC. In each case, when the concentration of each solvent was too low or too high, the polyphenol content decreased, underlining the importance of a precise balance to achieve high TPC. The combined desirability graph shows an optimization of the polyphenol content (PCT) with a desirability value of 1 for a PCT of approximately 1.9730 mg GAE/100 g, achieved at proportions of 75 % water, 12.5 % methanol, and 12.5 % ethanol. The linear relationship between desirability and TPC confirms that, to achieve a high TPC, it is essential to maintain these precise proportions. Imbalance or excessive variation in any of the solvents reduced the efficiency of polyphenol extraction (Fig. 4C).

4. Discussion

Plant compounds, such as terpenoids, phenolic compounds, and alkaloids, are the most important for food applications, including phenolic acids (hydroxybenzoic and hydroxycinnamic acids), polyphenols (hydrolyzable and condensed tannins), and flavonoids [8]. Solvent selection is an important step in the extraction of phenolic compounds and other bioactive compounds from fruits, vegetables, by-products, and their recovery from plant materials [18]. Depending on the solvent, the results showed that water, ethanol, and methanol were effective in extracting the largest quantities of TPC. In contrast, acetone and acetonitrile had the lowest

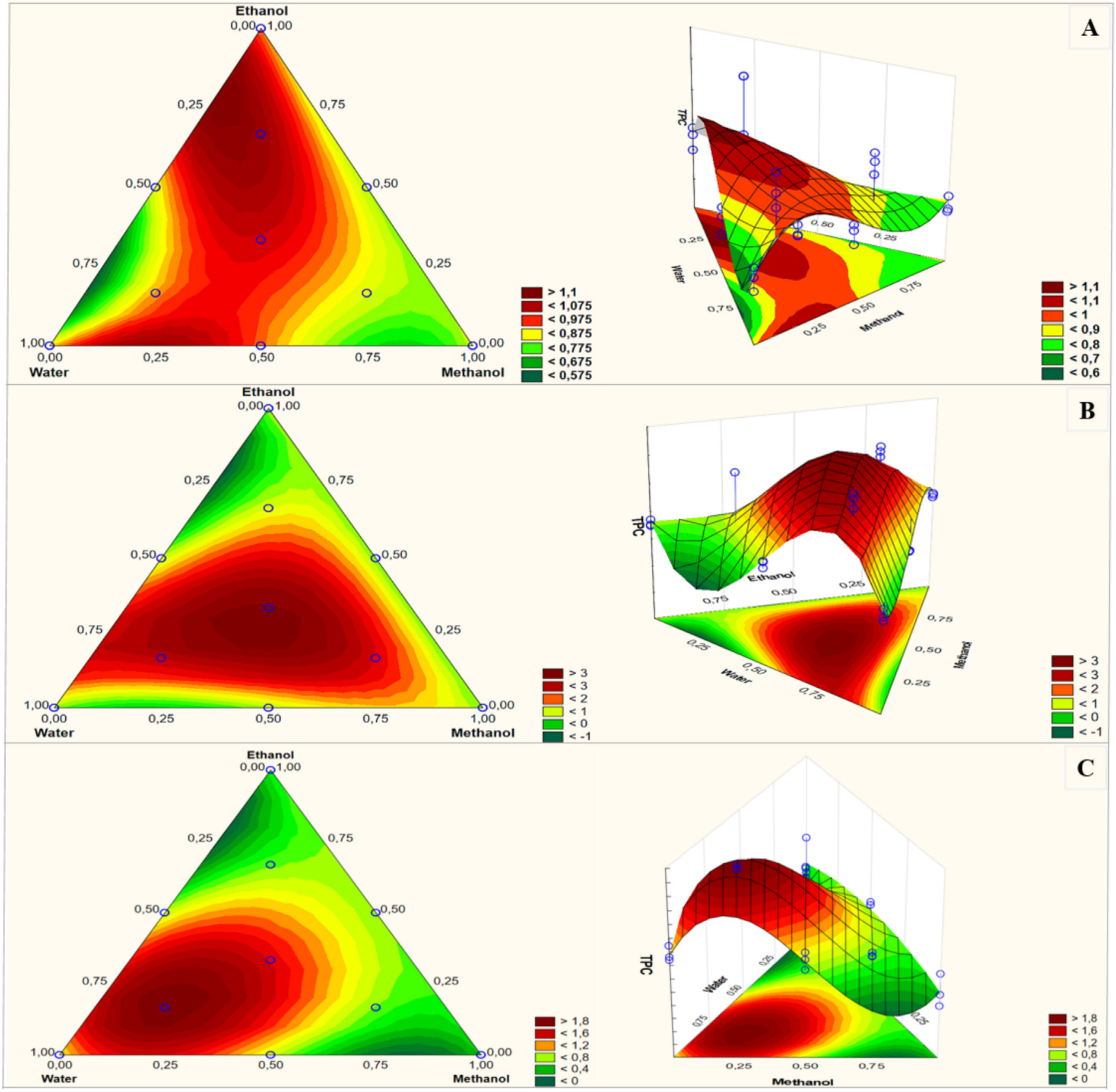


Fig. 3. Cubic response surface and contour plot indicating the effects of solvent mixture on TPC (mg GAE 100 g^{-1} DW). A: Mejhoul cultivar; B: Boufegouss cultivar and C: Bousthammi cultivar.

TPC values. Therefore, it is essential to develop a selective method for extracting phenolic compounds. The results obtained from TPC of dates extracted using different solvents ranged from 41.67 to 301.33 mg GAE.100 g^{-1} DW (Table 2 and Fig. 3). The maximum extraction target for phenolic compounds from dates, using distilled water was 278.33 mg GAE.100 g-1 DW. These results are lower than those obtained by Allaith [19] and Jdaini et al. [2], who found that the polyphenol content was 376 mg GAE 100 g DW for the cultivar 'Mabroom' and 316.72 mg GAE 100 g DW respectively. For the alone methanol extract, the TPC of dates was 257.23 mg GAE.100 g DW, which is higher than the values obtained by Souli et al. [20] and are very close to the results obtained by Jdaini et al. [2], are stated that the polyphenol content of the same solvent is 222.37 mg GAE/100 g DW. The phenolic compounds extracted by alone ethanol were 301.33 mg GAE.100 g DW, our results are lower than the results quoted by Bouhlali et al. [21], the values ranged from 537.07 mg GAE/100 g DW to 331.86 mg GAE/100 g DW for eight date palm cultivars from Morocco, and are similar to the results reported by Hasnaoui et al. [22] for date palm cultivars where the phenolic compound content ranged from 171.4 to 353.92 mg GAE/100 g DW. The water-ethanol-methanol mixture extracted 192.83 mg GAE.100 g DW from dates. These results are inferior to the results reported by Benmeddour et al. [23]; who found that 60 % acetone extracted nearly 493.15 mg GAE.100 g^{-1} DW from TPC, and are similar to the results quoted by Kchaou et al. [24] for Tunisian date varieties, which stated that the polyphenol content varied from 199.43 to 576.48 mg GAE/100 g DW.

Figure 3 shows the three-dimensional (3D) interaction contour plots based on the interactions between ethanol, methanol, and water. These three-dimensional response surface plots clearly show the impact of the

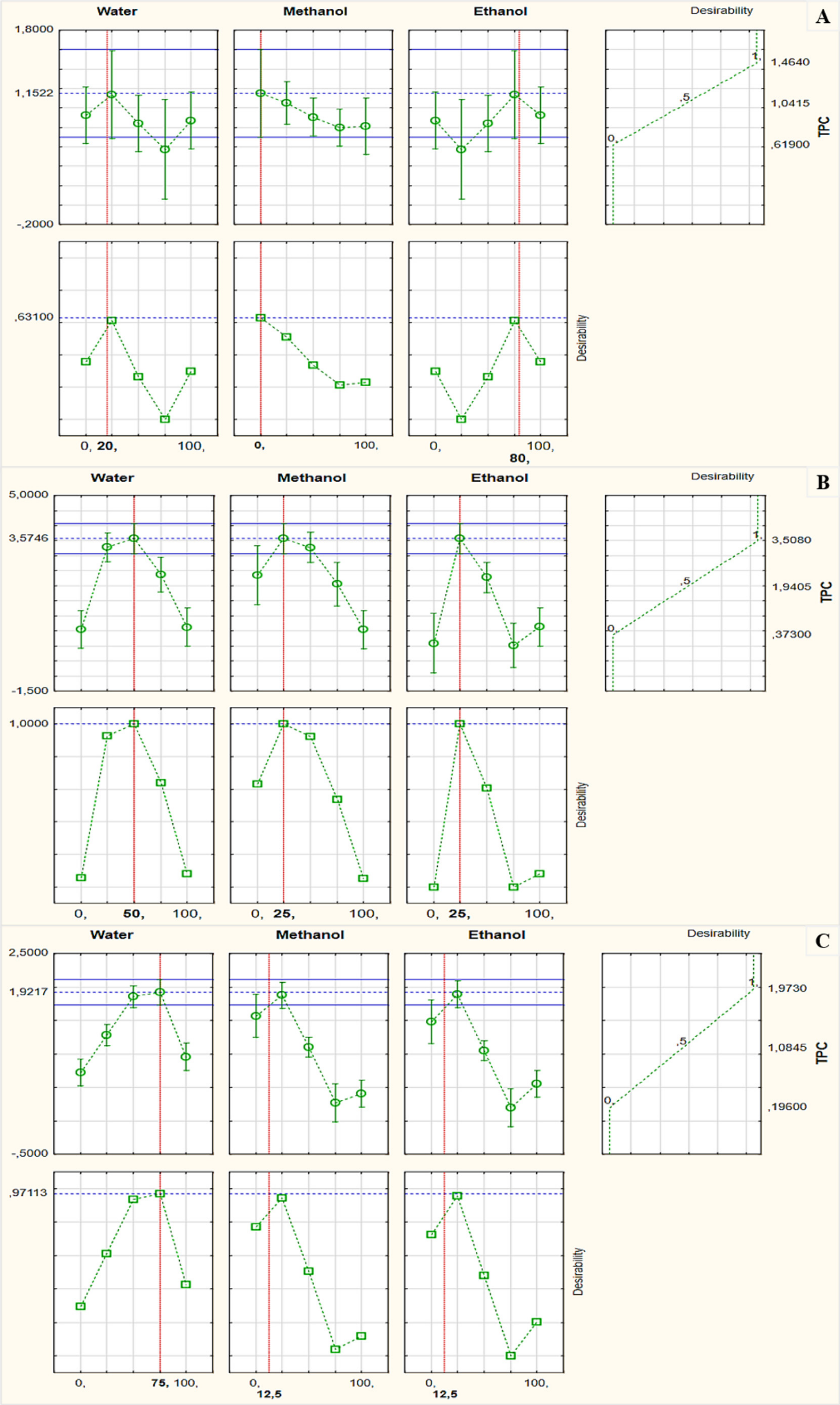


Fig. 4. Desirability results A: Mejhoul cultivar; B: Boufegouss cultivar and C: Bousthammi cultivar.

initial factors on the different responses. The use of desirability analysis to optimize TPC in the hydroalcoholic mixtures enabled us to identify the optimum conditions for each date cultivar. This approach not only confirmed the trends observed in the contour plots but also provided precise recommendations for solvent composition based on the specific characteristics of each cultivar. For the Mejhoul cultivar, a mixture containing 20 % water and 80 % ethanol provided the optimum yield of total phenolic compounds. This can be attributed to the moderate polarity of ethanol, which favors the extraction of soluble polyphenols from this matrix. The most efficient solvent combination for the Boufeggous cultivar is 50 % water, 25 % methanol, and 25 % ethanol. This profile probably reflects a better synergy between the solvent properties, enabling balanced extraction of polyphenols with varying polarities [25]. For the Bousthammi cultivar, the optimal blend was 75 % water, 12.5 % methanol, and 12.5 % ethanol. The use of a high-water content could indicate the predominance of hydrophilic polyphenols in this cultivar. This result also highlights the importance of water as a key component of the extraction process for this specific cultivar [26]. These results underline that solvent composition plays a crucial role in the extraction of phenolic compounds and that their efficiency is highly dependent on the biochemical peculiarities of each date cultivar. Furthermore, the variability of optimal solvent proportions between varieties suggests structural and/or solubility differences among polyphenols.

For a good extraction yield of water-soluble molecules and/or solvents, water and organic solvents are used to facilitate extraction [27]. It has been reported that mixed solvents, instead of single solvents, can be used to extract the maximum amount of phenolic compounds from plant samples. According to Cheng et al. [28] and Jayaprakasha et al. [29], water plays an important role in increasing the permeability of cell tissues, mass transfer by molecular diffusion, and extraction of water-soluble bioactive compounds. Nevertheless, mixing water with organic solvents creates a polar medium that is favorable for extraction [30], whereas the chemical properties of phenolic compounds change with the transition from simple to high polarity [2]. The results of several studies are not always consistent when estimating extraction efficiency due to differences in plant characteristics, such as plant species, fertilizers used, and growing season; the more the type of solvent and extraction technique used, the influence on the polyphenol content, and the change in the moisture content of the plant, thus affecting the expression of the results [31]. In general, several factors influence the extraction yield of phenolic compounds, such as temperature, time, and polarity of the solvent used, and their effects may be independent or interactive [32]. The use of a combination of solvents of varying polarities to extract significant quantities of bioactive compounds has been demonstrated in numerous studies [25,33], and it has been shown that the most efficient method for extracting phenolic compounds from plants is using mixtures of aqueous organic solvents [25]. Several studies have shown that TPC content is influenced by several factors, such as geographical and climatic factors [34], genetic factors, ripening stage, and storage conditions [35]. More than polyphenol content and biological activity varied according to several factors such as harvesting season, geographical location, experimental methods and the part of the plant studied [36].

Finally, the mixture design and triangular surfaces approach proved to be a valuable tool for multi-response optimization, making it possible to simultaneously maximize the phenolic compound yield while taking into account the different responses of the cultivars. These results could guide future work aimed at optimizing large-scale polyphenol extraction while offering prospects for the valorization of local date cultivars.

5. Conclusion

This study demonstrated the effectiveness of simplex-centroid design and desirability analysis in optimizing the extraction of total phenolic compounds (TPCs) from date fruits, considering the particularities of each cultivar. The results showed that the optimal solvent proportions varied according to the cultivar studied, highlighting the biochemical diversity of Moroccan dates. The Mejhoul cultivar gave its maximum yield with a mixture of 20 % water and 80 % ethanol, whereas for the Boufegouss cultivar, the ternary combination with equivalent proportions of 50 % water, 25 % ethanol, and 25 methanol is a better solvent for producing extracts with a high TPC content. In contrast, for the Bousthammi cultivar, the highest TPC value occurred with the ternary interaction composed of 75 % water, 12.5 % methanol, and 12.5 % ethanol.

Phenolic extracts derived from dates are recommended as superior alternatives to chemical food additives. The results of this study confirm the importance of a rigorous selection of solvents and their combinations to maximize the extraction of polyphenols, which are bioactive compounds of major interest for their antioxidant properties. This methodological approach is a valuable tool for the valorization of local date palm varieties and provides a solid basis for industrial and nutritional applications. Future studies could explore other bioactive compounds present in these varieties and assess their potential in various sectors such as pharmacology, functional foods, and cosmetics.

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CRediT authorship contribution statement

Abdelfattah Goubi: Writing – review & editing, Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Dounia Amghar:** Writing – review & editing, Visualization, Software, Methodology, Investigation, Formal analysis. **Abdellatif Boutagayout:** Writing – review & editing, Visualization, Validation, Software, Formal analysis, Data curation. **Houria Nekhla:** Writing – review & editing, Visualization, Software, Methodology, Formal analysis. **Hicham Elidrissy:** Writing – review & editing, Validation. **Lahsen El Ghadraoui:** Resources, Writing - Review, Editing, and Co-Supervision. **Raja Guemmouh:** Writing – review & editing, Validation, Supervision, Project administration, Methodology, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare no conflict of interest.

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