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Microwave-Vacuum Extraction Technique as a Green and Clean Label Technology: Kinetics, Efficiency Analysis, and Effect on Bioactive Compounds

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Abstract

Grape pomace is a rich source of bioactive compounds and dietary fiber. This study aims to valorize the grape pomace by microwave-vacuum-assisted drying and extraction, which is a novel, green, and clean label technology. The drying and extraction of bioactive compounds from the grape pomace was optimized using response surface methodology. Box-Behnken design was used for three process variables, i.e., time, power, and vacuum levels. The highest drying rate was observed (5.53 g/100 g min after 10 min of drying) at the combination of 80 W and 20 inHg. This combination significantly reduced the drying time (25%) and resulted in the highest yield (64.5%) of bioactive compounds. Equally, changes in moisture ratio behavior were rapid under these processing conditions. Furthermore, Midilli model ($R^2 = 0.999$, RMSE = 0.002, SSE = 3.71×10^{-6}) was the best to justify the fitness of experimental values with predicted values. In addition, the diffusion coefficient, activation energy, and extraction yield were increased with increase in power and pressure. The concentration of bioactive components was higher in dried pomace compared to the extract. The extraction was successfully achieved without the use of solvent and the characteristics of extracted phenolics remained unaltered. Based on these findings, the microwave-vacuum-assisted drying and extraction process can be claimed as a sustainable approach.

Keywords Grape pomace · Microwave-vacuum drying · Kinetics modeling · Bioactive compounds · Green extraction

Introduction

Grapes, scientifically known as "*Vitis vinifera* L.," is a fruit of high economical value that is produced worldwide. It is a rich source of antioxidants, vitamins, minerals, and other micronutrients. In addition to the fresh consumption, it is also used to produce wine and juice. This process produces a huge waste (~ 18 million tone) in the form of pomace (Moro et al., 2021). Grape pomace (20–30% of the weight of grapes) consists of stem, skin, seeds, and small proportion of juice (Bao et al. 2020). A small amount of pomace is used as animal feed and the rest is either utilized as fertilizer or submitted to incineration and landfill (Drevelegka and Goula 2020). Disposal of large amount of pomace may have severe environmental impacts, such as soil and water pollution, soil acidification, and oxygen depletion in soil (Nakov et al. 2020).

Nevertheless, various studies on the composition of grape pomace have revealed that it is a source of macronutrients (especially dietary fiber) and contains bioactive components (BACs) (Goula et al. 2016; Kwiatkowski et al. 2020). Among these BACs, phenolic acids, pro-anthocyanidins, flavanols, anthocyanins, flavonols, and stilbenes are the most common. These BACs have several human health benefits, including prevention of molecular oxidation, inhibition of heart disease, anti-inflammatory, and anti-carcinogenic action (Averilla et al. 2019; Sies and Jones 2020). Thus, efforts are being made to extract these functional compounds through various extraction techniques (El Darra et al. 2013; Bubalo et al. 2016). These techniques use various types of solvents and pose a threat to environment, while increasing processing time and energy consumption. These traditional

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techniques are also inefficient to explore the potential of such valuable agro-food by-products. This has led to the search for rapid and cost-effective technique for the of extraction bioactive components (Moro et al. 2021).

In this regard, microwave has potential for the extraction of BACs without the use of solvents. This technique has been used for the extraction of BACs from various plant matrix including fenugreek, ginger, and onion (Brahim et al. 2014; Drevelegka and Goula 2020; Kwiatkowski et al. 2020; Khan et al. 2021). It is an efficient, economical, and clean alternative due to it speed, low energy consumption, and lack of solvents use (Khan et al. 2021; Alvi et al. 2022); however, to the best of our knowledge, the use of microwave with vacuum has not been investigated for extraction and drying of grape pomace. The aim of our research was to optimize the microwave-vacuum technique for the extraction of bioactive compounds with simultaneous drying of grape pomace. Subsequently, the evaluation of phenolic compounds in the extract, the antioxidant activity of pomace before and after the extraction was carried out. Moreover, physicochemical analysis, process efficiency, and energy utilization were determined.

Materials and methods

Preparation of Sample

Mature grapes (Sundar khani) were purchased from the local market of Faisalabad (Pakistan) and subjected to preparatory operations such as trimming of rachis and peduncle, sorting for damaged and overripe grapes. Then, a washing was carried with tap water to remove dust and dirt. The fruit was then blended and the resulting mixture was poured over the sieve to separate the juice (permeate) and pomace (retentate). The pomace was placed in the refrigerator at 10 °C for 3 h to separate the juice that is not well bound. Then, extraction and drying were carried out, followed by physicochemical analysis.

Drying and Extraction Process

The drying of grape pomace with simultaneous extraction of bioactive compound was carried out in a specifically designed instrument, as reported earlier by Khan et al. (2021). The grape pomace sample weighing 100 g was placed in the reactor. The process variables like power (30, 50, and 80 W), vacuum (10, 15, and 20 inHg), and time (5, 10, and 15 min) were chosen as per Box-Behnken design (BBD). This design was used to optimize the drying conditions, which are coded in Table 1. During the process, the water flow rate through the condenser (16 °C) was maintained at 100 mL/min to assist in the condensation of the vapors. The dried pomace and recovered vapors were stored in polyethylene bottles at room temperature until further analysis.

Drying Rate

Changes in weight of pomace as a function of time during drying was used in the following equation to calculate the drying rate (g moisture/100 g min):

Table 1 Establishment of drying conditions for grape pomace with their codes using response surface methodology

Sr. No	Coded values			Actual values			Drying rate (g/100 g min)	Moisture ratio
	Time	Vacuum	Power	Time (min)	Vacuum (inHg)	Power (W)		
1	0	0	0	10	15	50	2.587	0.782
2	1	0	1	15	15	80	4.965	0.260
3	0	1	1	10	20	80	5.527	0.450
4	−1	0	−1	5	15	30	0.400	0.980
5	−1	−1	0	5	10	50	1.267	0.940
6	1	−1	0	15	10	50	2.500	0.690
7	0	0	0	10	15	50	2.587	0.782
8	−1	1	0	5	20	50	2.187	0.836
9	1	0	−1	15	15	30	0.600	0.890
10	0	1	−1	10	20	30	0.73	0.930
11	0	−1	−1	10	10	30	0.53	0.950
12	0	−1	1	10	10	80	4.733	0.530
13	1	1	0	15	20	50	3.105	0.672
14	0	0	0	10	15	50	2.587	0.782
15	0	0	0	10	15	50	2.587	0.782
16	0	0	0	10	15	50	2.587	0.782
17	−1	0	1	5	15	80	3.453	0.756

$$\text{Dryingrate(DR)} = \frac{m_t - m_{t+dt}}{\mathrm{d}t} \quad (1)$$

Here, m_t (g) is the moisture in the product at time t, m_{t+dt} (g) is the moisture at time $t+dt$, and t and $t+dt$ (min) are the initial time and time after specific interval, respectively.

Moisture Ratio

Moisture ratio, the relative amount of moisture removed, was calculated by the following equation:

$$\text{Moisture ratio(MR)} = \frac{m_t - m_e}{m_o - m_e} \quad (2)$$

Here, m_o, m_t and m_e are the moisture contents initially, at time t and at equilibrium, respectively. Moisture ratio calculated from the above equation was compared with different model Eqs. (3)–(6) as given below.

Model Equations

$$\text{Henderson and Pabis} \quad \text{MR} = \exp(-kt) \quad (3)$$

$$\text{Page} \quad \text{MR} = \exp(-kt^n) \quad (4)$$

$$\text{Logarithmic} \quad \text{MR} = \alpha \times \exp(-kt) + \beta \quad (5)$$

$$\text{Midilli} \quad \text{MR} = \alpha \times \exp(-kt^n) + \beta t \quad (6)$$

Diffusion Coefficient

Diffusion coefficient in a unsteady-state drying process was determined by Fick's law of diffusion, written as;

$$\text{MR} = \frac{m_t - m_e}{m_o - m_e} = \frac{8}{\pi^2} exp(-\alpha) \quad (7)$$

Diffusion coefficient was calculated from the slope of line (α) drawn between ln (MR) and time as;

$$\alpha = \left(\frac{\pi^2 Dt}{4L^2}\right) \quad (8)$$

Here, D, t and L are effective diffusion coefficient (m^2/s), time (s) and thickness (m) of the sample layer distributed in the drying chamber, respectively.

Antioxidant Activity

The antioxidant activity of dried grape pomace and vapor extract were calculated using the DPPH assay (Khan et al. 2020). The reaction mixture was prepared by adding 0.5 mL of extract (ethanolic/microwave) in 0.3 mL of 0.5 mM DPPH solution and 3 mL of ethanol. For vapor extracts, 50 µL of vapor extract was mixed with 5 mL of 0.004% DPPH solution. The mixture was placed in the dark for 30 min and the absorbance was measured at 515 nm using UV/vis spectrophotometer (STA-8200 V, Stalwart Analytics, Germany). DPPH activity (%) was calculated as:

$$\text{Antioxidant activity (\%)} = \frac{A_o - A_s}{A_o} \quad (9)$$

Here, A_s and A_o are the values of absorbance of sample and DPPH solution, respectively.

Total Phenolic Contents

The total phenolic contents in grape pomace and vapor extract was estimated using the Folin-Ciocalteu method (Loizzo et al. 2019). 0.5 mL of prepared extract (0.8 g pomace/L ethanol) and 0.5 mL of vapors were separately mixed with 2.5 mL of tenfold diluted Folin reagent and 2 mL of sodium carbonate (40 g/L). The absorbance of the prepared mixture was measured at 765 nm after keeping the samples in dark for 2 h at room temperature. The total phenolic contents were quantified in terms of mg gallic acid equivalent (GAE) per gram of grape pomace and per milliliter of vapor extract by comparing the absorbance with the standard curve of gallic acid.

Total Flavonoid Contents

Total flavonoids in dried grape pomace and extract were measured following the protocol of (Loizzo et al. 2012). 0.5 mL of the sample (200 g/L) was mixed with 0.3 mL of sodium nitrite (5%) and aluminum chloride (10%). Distilled water was added to make a volume of 5 mL of the solution. Two milliliters of sodium hydroxide (NaOH, 1 M) was added in the solution. All samples were placed at room temperature before absorbance was measured at 415 nm in a UV/vis spectrophotometer (STA-8200 V, Stalwart Analytics, Germany). The quercetin standard curve was used to quantify the total flavonoids and was expressed as mg of quercetin equivalent (QE) per gram of dried pomace and per milliliter of extract.

Fourier Transform Infrared (FTIR) Spectroscopy

The samples were analyzed to identify functional groups using an FTIR spectrometer (Bruker Tensor 27) with attenuated total reflector (ATR), DLATGS detector using spectral range of 400–6000 cm^{-1} with a standard KBr beam splitter (Pasha et al. 2021). The samples were analyzed and the spectra peaks interpreted via OPUS software (Bruker Optik GmbH, Ettlingen).

Encapsulation of Extract

The condensed extract, obtained during drying process, was encapsulated in sodium alginate (2%, w/v) solution. The sodium alginate solution and the extract were mixed under stirring (200 rpm) and heating (70 °C) to facilitate thorough dispersion. The solution was dripped through the kit (Hydocs, pore size 0.45 mm) into calcium chloride solution (1%, w/v). The drip speed was maintained at 4.54 mL/min with the 15 cm distance between the kit nozzle and the solution. The resulting capsules were left in the calcium chloride solution for 10 min. Then, the capsules were separated and washed with deionized water to remove excess calcium and prevent complexation process (da Silva Carvalho et al. 2019). Additionally, the encapsulation efficiency of the alginate-extract capsules was measured by dividing the TPC of the capsules by the TPC of extract (Stojanovic et al. 2012).

$$\text{Encapsulation Efficiency (EE)} = \frac{TPC_m}{TPC_s} \tag{10}$$

Here, TPC_m is the total phenolic contents in the microcapsules and TPC_s is the total phenolic contents in the polymer-extract solution.

Statistical Analysis

In this study, Box-Behnken design (BBD) was chosen for modelling the process variables (power, time, and pressure). The response surface methodology (RSM) was applied to evaluate the influence of power and pressure on the drying rate and moisture ratio of grape pomace. The regression models were constructed for three parameters using the experimental design presented in Table 1. Finally, a comparison between the estimated with predicted values was carried out through R^2, RMSE, SSE, chi-square, and RPD value.

$$\text{Root Mean Square Error (RMSE)} = \sqrt{\frac{1}{N}\sum_{i=1}^{n}\left(V_{exp,i} - V_{model,i}\right)^2} \tag{11}$$

$$\text{Sum of Square Error(SSE)} = \frac{1}{N}\sum_{i=1}^{n}\left(V_{exp,i} - V_{model,i}\right)^2 \tag{12}$$

$$\text{Chi Square } (\chi^2) = \frac{1}{N - n_p}\sum_{i=1}^{n}\left(V_{exp,i} - V_{model,i}\right)^2 \tag{13}$$

$$\text{Relative Percent Deviations (RPD)} = \frac{100}{N}\sum_{i=1}^{n}\left|\frac{V_{exp,i} - V_{model,i}}{V_{exp,i}}\right| \tag{14}$$

Results and Discussions

Drying Rate

A model equation for drying rate was obtained by RSM analysis controlling for the processing variables and expressed in Eq. (15). The ANOVA results indicated that the *P*-value (< 0.0001) was lowest value and revealed that model equation was highly significant at $P \leq 0.05$ (Table 2). The quadratic model had a coefficient of determination (R^2) of 0.989; the adjusted R^2 of 0.975 and predicted R^2 of 0.809 were close as the difference was ~ 0.180. The adjusted R^2 is the variance proportion in the output that is predictable from the input that in the real sense had effects on the output, whereas the predicted R^2 is an indicator of how well a regression model predicts the outputs for new observations (Chakraborty et al. 2011). Thus, statistical evaluation indicates that the model equation can be used to predict the maximum values of drying rate.

$$\begin{aligned}\text{DR} = {} & 0.004\text{V}^2 - 0.0004\text{P}^2 - 0.017\text{T}^2 + 0.001\text{PV} - 0.003\text{TV} \\ & + 0.002\text{TP} - 0.083\text{V} + 0.081\text{P} + 0.352\text{T} - 3.636\end{aligned} \tag{15}$$

The DR of grape pomace (subjected to different levels of power, vacuum, and time) is plotted in Fig. 1. The DR increased with increasing power levels (Fig. 1a). It was the lowest (between 1.1 and 1.2 g/100 g min after 30 min for all pressure levels) at 30 W and continued to increase even after 30 min of processing. This may be due to slow heating at this power. With the increase in power (30 to 50 W), the DR value reached to 1.25 g/100 g min within 5 min, which was the higher value than 30 W. Moreover, the drying time was 6 times reduced compared to the lowest power level. Similarly, the DR reached at 3.16 g/100 g min in 3 min at 80 W, which was the highest value of DR in the lowest time of processing.

Presumably, the increase in power rapidly excited the physically bound water molecules and caused them to leave off the surface of pomace. This reduced the drying time by about threefold at 80 W compared to 30 W. After the maximum drying rate (5.53 g/100 g min) was reached in 10 min at 80 W, further processing resulted in reduction of drying rate as moisture contents in pomace were reduced. Similar trends have already been reported in literature, and thus, increasing the power level significantly increased the DR and decreased the processing time from 30 to 3 min.

The DR increased significantly with increasing vacuum level inside the drying chamber (Fig. 1b). The combined effect of power and vacuum revealed that drying rate was uppermost at higher pressure levels. The maximum value observed was 5.53 g/100 g min after 10 min of drying at 20 in Hg and 80 W (Fig. 1c). This could be due to the vacuum inside the chamber which rapidly removed all the moisture produced during drying process and maintained the moisture

Table 2 ANOVA for quadratic model of drying rate and moisture ratio

Source	Sum of square	df	Mean square	*F*-value	*p*-value	
Drying rate						
Model	37.75	9	4.19	69.09	< 0.0001	Significant
A-time	2.41	1	2.41	39.69	0.0004	Significant
B-power	19.32	1	19.32	318.18	< 0.0001	Significant
C-pressure	0.7106	1	0.7106	11.71	0.0111	Significant
AB	0.3939	1	0.3939	6.49	0.0383	
AC	0.0248	1	0.0248	0.4086	0.5430	
BC	0.0715	1	0.0715	1.18	0.3137	
A^2	0.7561	1	0.7561	12.45	0.0096	
B^2	0.1974	1	0.1974	3.25	0.1144	
C^2	0.0435	1	0.0435	0.7168	0.4252	
Residual	0.4250	7	0.0607			
Lack of fit	0.4250	3	0.1417			
Pure error	0.0000	4	0.0000			
Cor total	38.18	16				
Drying rate $R^2 = 0.989$		**Adjusted $R^2 = 0.975$**			**Predicted $R^2 = 0.975$**	
Moisture ratio						
Model	0.5802	9	0.0645	319.52	< 0.0001	Significant
A-time	0.0538	1	0.0538	266.60	< 0.0001	
B-power	0.1501	1	0.1501	744.19	< 0.0001	
C-pressure	0.0083	1	0.0083	41.38	0.0004	
AB	0.0440	1	0.0440	218.08	< 0.0001	
AC	0.0018	1	0.0018	9.06	0.0197	
BC	0.0008	1	0.0008	4.10	0.0826	
A^2	0.0001	1	0.0001	0.4416	0.5276	
B^2	0.0018	1	0.0018	9.14	0.0193	
C^2	0.0000	1	0.0000	0.0814	0.7837	
Residual	0.0014	7	0.0002			
Lack of fit	0.0014	3	0.0005			
Pure error	0.0000	4	0.0000			
Cor total	0.5816	16				
$R^2 = 0.998$		**Adjusted $R^2 = 0.994$**			**Predicted $R^2 = 0.961$**	

gradient inside the drying chamber. The similar trend was reported by Suna (2019) during the vacuum drying of medlar fruit leather.

While pressure and power levels were important factors controlling the rate of moisture removal, a falling rate period started after 30 min of drying at 30 W (Fig. 1d). At higher power levels, the drop-off period started earlier than the low power levels (12 and 15 min for 80 and 50 W, respectively). This could be associated with the increase in temperature inside the drying chamber with increasing power. These findings were in line with the results of those who used this technique for the drying of onion and ginger. Therefore, it can be concluded that higher power (P) and vacuum levels (V) can be efficiently employed to improve the drying rate and rapidly remove the moisture contents form the product. The optimized conditions for the drying rate were 80 W, 20 inHg, and 10 min.

Moisture Ratio

Moisture ratio describes the relative moisture loss of the product and was used to determine the drying kinetics of grape pomace. A model equation was obtained by RSM analysis including three processing variables and expressed in Eq. (16). The ANOVA results indicated that *P*-value (< 0.0001) had the lowest values and revealed that the model equation was highly significant at $P \leq 0.05$ (Table 2). The quadratic model had R^2 of 0.998, the adjusted R^2 of 0.994, and predicted R^2 of 0.961 were quite close as the difference was ~ 0.037 (Chakraborty et al. 2011). Thus, the statistical

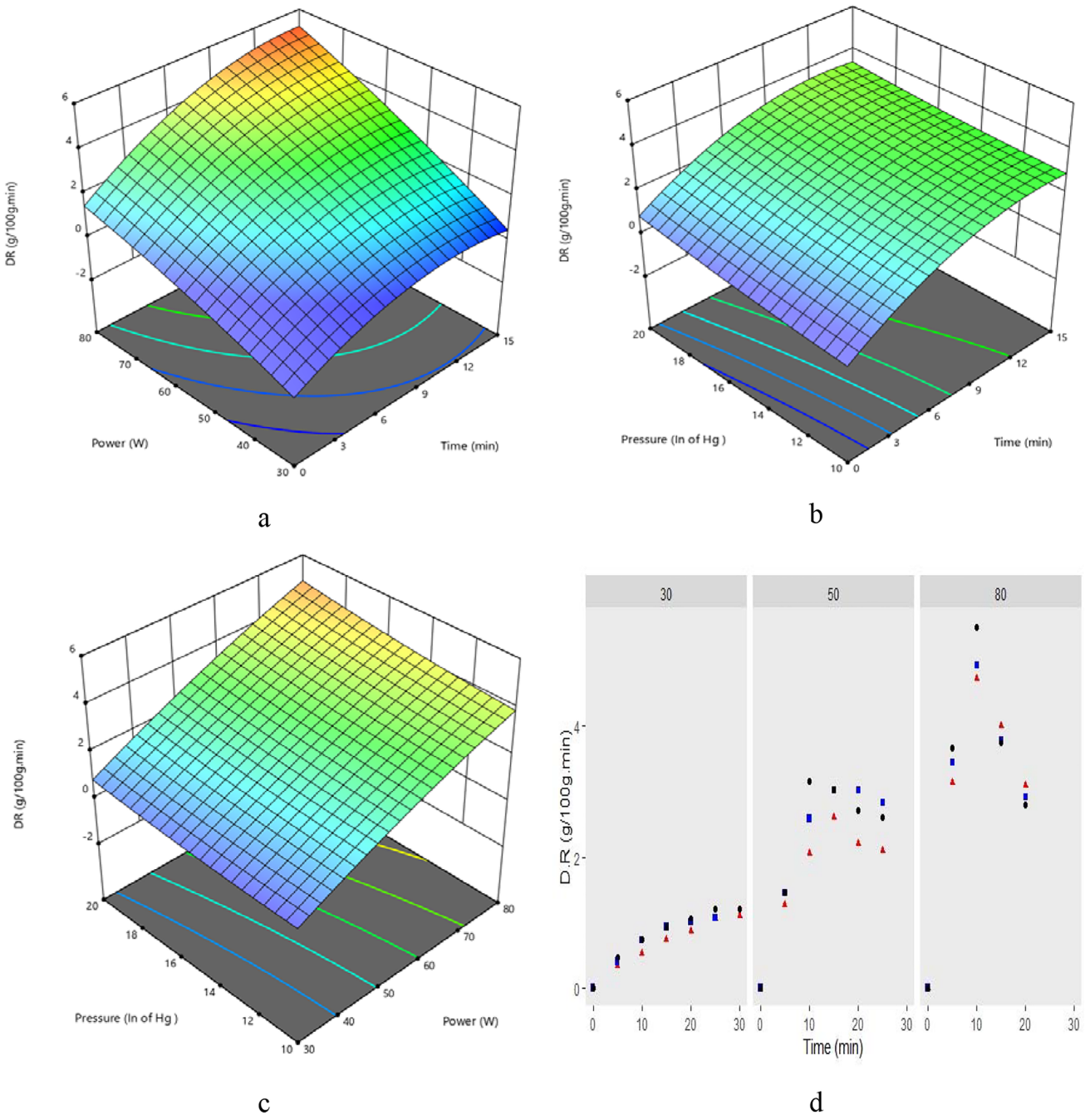

Fig. 1 A combined effect of different powers, and time on the drying rate of pomace subjected to varying vacuum levels (triangle, square, and circle represents vacuum levels 10, 15, and 20 in Hg, respectively)

evaluation indicates that the model equation can be used to predict the maximum values of drying rate.

$$\begin{aligned} MR = {} & 1.051 + 2.09 \times 10^{-3}T + 5.13 \times 10^{-3}P - 5.74 \times 10^{-3}V \\ & - 8.31 \times 10^{-4}TP + 8.55 \times 10^{-4}TV \\ & - 1.14 \times 10^{-3}PV + 1.84 \times 10^{-4}T^2 \\ & - 3.50 \times 10^{-5}P^2 - 7.90 \times 10^{-5}V^2 \end{aligned} \quad (16)$$

The variations in MR at different pressure and power levels throughout the drying process were sketched in Fig. 2. At 30 W, MR were 0.71 after 30 min of drying, and it was quickly reduced to minimum value of 0.15 after 20 min of drying at 80 W, while maintaining a vacuum of 20 inHg (Fig. 2d).

The vacuum facilitated drying and caused the lowest MR values at higher vacuum levels (20 inHg) at the

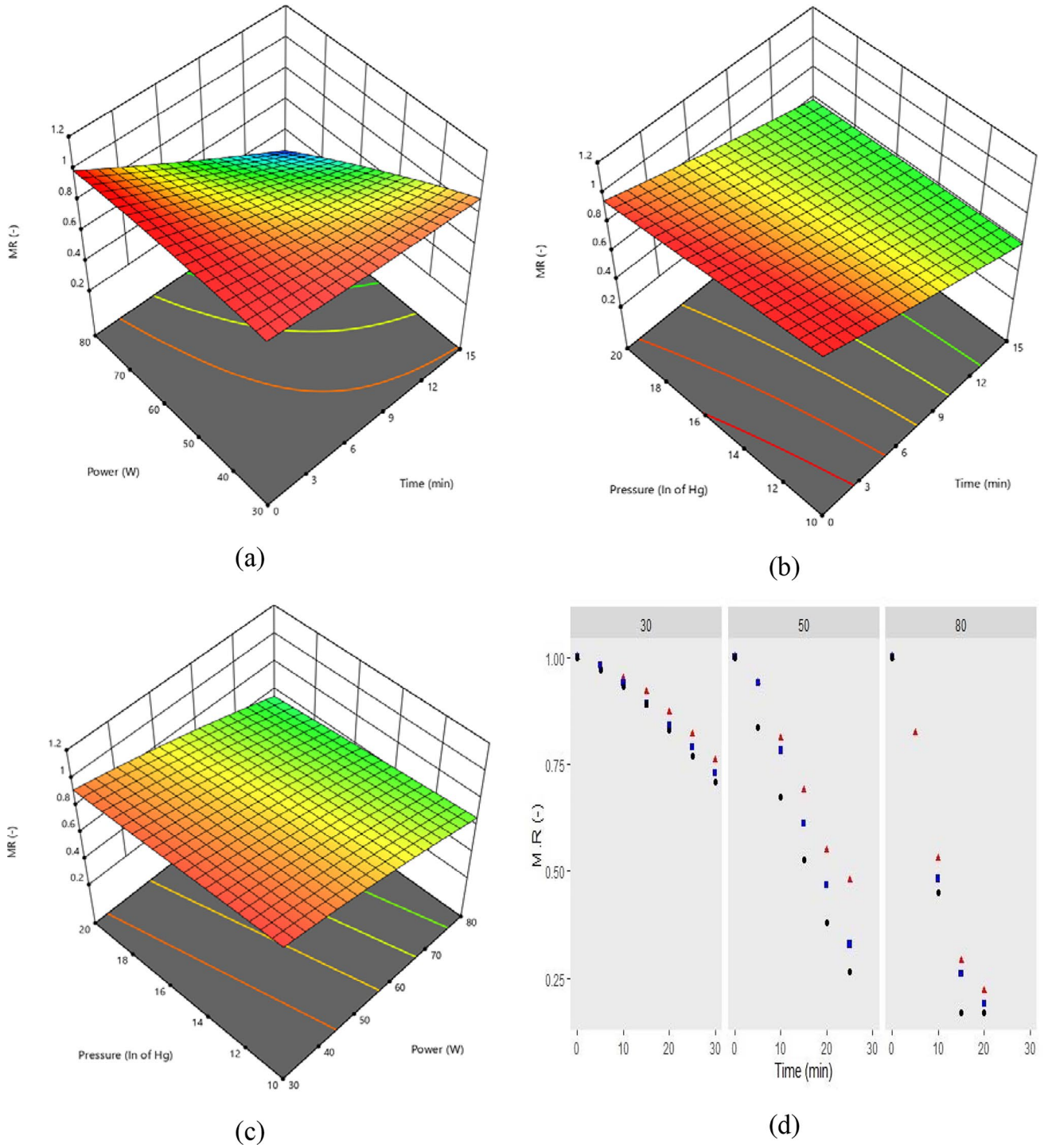

Fig. 2 A combined effect of different levels of power, time and vacuum (triangle, square, and circle represent the different vacuum level 10, 15, and 20 inHg, respectively) on moisture ratio of grape pomace.

constant microwave power. For instance, MR was observed as 0.29 at 10 inHg and was reduced to 0.17 at 20 inHg at 80 W power. This resulted in 2 times reduction of processing time. The maximum reduction (45%) in MR was observed at 80 W and 20 inHg during 5- to 10-min interval of drying. Higher power and pressure might remove the moisture faster, which then reduced the MR value. These results were in agreement with those who applied the vacuum-assisted microwave process for drying of dragon fruit.

The MR was predicted using different model equations and the results were compared with the experimental values. Statistical analysis (Table 4) revealed that the Midilli model was the best-fitting model, with a high R^2 (0.999) and lowest RSME (0.002) and SSE (3.71×10^{-6}) values followed by the logarithmic, and Page models for all the treatments. Thus, the Midilli model was the best fit to predict the behavior of MR (Table 3).

Antioxidant Activity and Phenolic Compounds

The phenolic compounds (DPPH, TPC, and TFC contents) of dried pomace and vapors are compared in Fig. 3. The DPPH contents of dried pomace were three times higher than those of fresh pomace (Fig. 3a). A non-significant effect of process variables (power and vacuum) was observed on DPPH contents. Besides, the TFC contents of dried pomace increased with increasing power up to 50 W. Then, it started to decrease with further increase in power level (Fig. 3e).

In dried grape pomace, TPC contents linearly increased with increasing vacuum and power levels (Fig. 3c). The TPC contents were higher in dried pomace compared to the fresh one. Furthermore, the maximum TPC values were observed at the highest power and vacuum levels. It can be observed that pomace revealed an improvement of 66% in TPC

Table 3 Fit parameters of the values of moisture ratio in different statistical models

Model	Power	Pressure	k	n	α	β	R^2	RSME	SSE	Chi^2	RPD (%)
Henderson and Pabis	30	10	0.00690				0.9454	0.0146	2.12×10^{-4}	2.55×10^{-4}	1.32
	30	15	0.00857				0.9693	0.0127	1.62×10^{-4}	1.95×10^{-4}	1.15
	30	20	0.00924				0.9600	0.0158	2.50×10^{-4}	3.01×10^{-4}	1.49
	50	10	0.02670				0.9589	0.0387	1.50×10^{-3}	1.80×10^{-3}	4.78
	50	15	0.03517				0.9289	0.0647	4.18×10^{-3}	5.02×10^{-3}	1.30
	50	20	0.04559				0.9823	0.0337	1.13×10^{-3}	1.36×10^{-3}	6.56
	80	10	0.06858				0.9578	0.0610	3.80×10^{-3}	4.75×10^{-3}	11.45
	80	15	0.07720				0.9788	0.0442	1.95×10^{-3}	2.44×10^{-3}	3.75
	80	20	0.08730				0.9651	0.0604	3.65×10^{-3}	4.57×10^{-3}	15.92
Page	30	10	0.00137	1.542			0.9975	0.0031	9.58×10^{-6}	1.44×10^{-5}	0.25
	30	15	0.00293	1.362			0.9973	0.0038	1.44×10^{-5}	2.16×10^{-5}	0.26
	30	20	0.00251	1.439			0.9978	0.0037	1.37×10^{-5}	2.05×10^{-5}	0.33
	50	10	0.00786	1.424			0.9956	0.0126	1.59×10^{-4}	2.38×10^{-4}	1.53
	50	15	0.00518	1.669			0.9992	0.0069	4.78×10^{-5}	7.17×10^{-5}	0.79
	50	20	0.02104	1.277			0.9987	0.0091	8.27×10^{-5}	1.24×10^{-4}	1.65
	80	10	0.02130	1.463			0.9926	0.0261	6.70×10^{-4}	1.13×10^{-3}	6.87
	80	15	0.03500	1.317			0.9964	0.0182	3.31×10^{-4}	5.53×10^{-4}	5.36
	80	20	0.03480	1.378			0.9862	0.0380	1.44×10^{-3}	2.40×10^{-3}	14.65
Logarithmic	30	10	−0.04557		−0.086	1.086	0.9988	0.0021	4.46×10^{-6}	1.78×10^{-6}	0.20
	30	15	−0.02916		−0.198	1.198	0.9977	0.0035	1.21×10^{-5}	2.42×10^{-5}	0.32
	30	20	−0.03570		−0.161	1.161	0.9993	0.0020	4.15×10^{-6}	8.30×10^{-6}	0.20
	50	10	−0.00517		−4.024	5.042	0.9895	0.0195	3.82×10^{-4}	7.64×10^{-4}	2.48
	50	15	−0.01559		−1.483	2.507	0.9922	0.0214	4.59×10^{-4}	9.18×10^{-4}	2.92
	50	20	0.01486		2.384	−1.381	0.9998	0.0028	7.98×10^{-6}	1.60×10^{-5}	0.47
	80	10	0.03150		1.792	−0.767	0.9805	0.0419	1.70×10^{-3}	4.40×10^{-3}	9.46
	80	15	0.04890		1.365	−0.350	0.9903	0.0298	8.88×10^{-4}	2.22×10^{-3}	7.83
	80	20	0.05980		1.288	−0.268	0.9764	0.0496	2.46×10^{-3}	6.16×10^{-3}	17.91
Midilli	30	10	0.00006	2.280	1.000	−39.230	0.9990	0.0019	3.71×10^{-6}	1.11×10^{-5}	0.17
	30	15	0.00028	1.829	0.999	−0.005	0.9981	0.0032	1.00×10^{-5}	3.01×10^{-5}	0.29
	30	20	0.00006	2.280	1.000	−59.200	0.9994	0.0019	3.71×10^{-6}	1.11×10^{-5}	0.17
	50	10	0.00841	1.571	0.999	0.008	0.9986	0.0071	5.10×10^{-5}	1.53×10^{-4}	0.89
	50	15	0.00548	1.701	1.000	0.002	0.9995	0.0052	2.66×10^{-5}	7.99×10^{-5}	0.83
	50	20	0.02301	1.097	1.000	−0.008	0.9999	0.0013	1.77×10^{-6}	5.30×10^{-6}	0.22
	80	10	0.01280	1.803	0.998	0.008	0.9993	0.0079	6.17×10^{-5}	3.08×10^{-4}	1.78
	80	15	0.02580	1.531	0.998	0.005	0.9989	0.0098	9.60×10^{-5}	4.80×10^{-4}	2.50
	80	20	0.02090	1.691	0.994	0.006	0.9919	0.0290	8.40×10^{-4}	4.20×10^{-3}	9.77

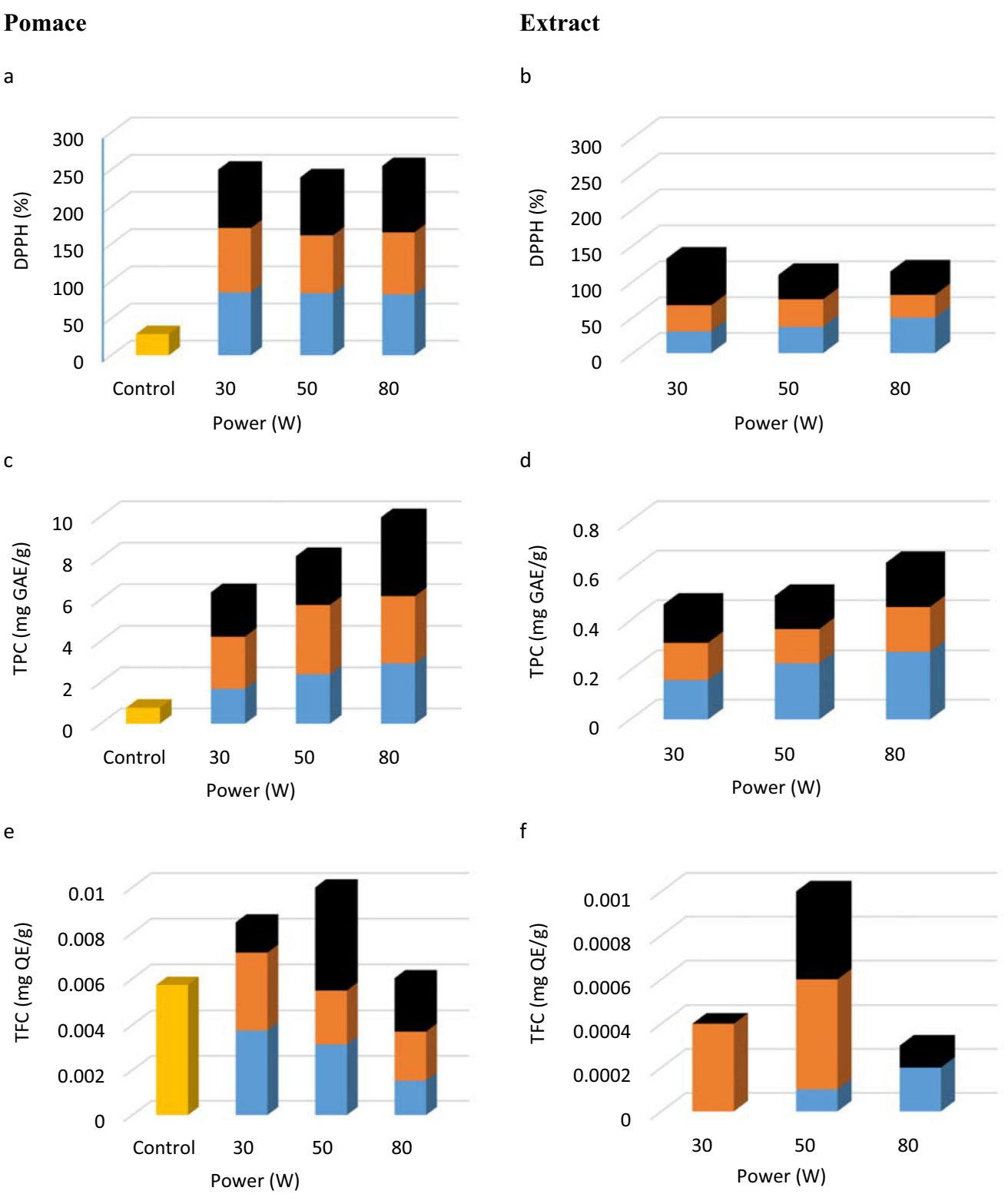

Fig. 3 Effect of vacuum and power on phenolic contents of dried pomace and vapors recovered from grape pomace with MADE technique; control, 10 inHg, 15 inHg, and 20 inHg

contents when the power and vacuum levels were changed from low to high. This can be attributed to the fact that the increase in power resulted in greater moisture removal over time and increased the solid contents of the pomace. This led to an increase in the value of phenolic compounds in the dried pomace and retained the bioactive compounds in pomace. Similarly, the TFC contents were also higher in the dried pomace than in the fresh pomace. Moreover, it is evident that pomace has better phenolic activity than solvent extraction.

Phenolic contents in vapors/extract (obtained by condensation) followed the trend of pomace (Fig. 3b, d, and f). However, the values were ten times lower in vapors compared to pomace. This indicates that most of the phenolic compounds were retained in pomace can be used as functional ingredients due to higher phenolic contents. Thus, the results revealed that dried pomace had higher values for all three phenolic contents. In addition, the extraction was higher without altering the phenolic performance.

Fourier Transform Infrared (FTIR) Spectroscopy

The functional groups of chemical compounds and their mode of vibrational motion in extract of grape pomace were examined using FTIR technique (Fig. 4).

The wavenumber ranges to identify various functional groups and their vibrational mode in the pomace extract are illustrated in Table 4. The peaks in the range of 3200–3400 cm^{-1} showed the presence of stretching of the hydroxyl group (—OH str) as discussed in (Olalere et al. 2021). The antisymmetric vibrational motion of the methyl group (—CH3) was observed in the range of 2952–2972 cm^{-1}. The ranges of wavenumber 2500–3300 cm^{-1} and 900–950 cm^{-1} indicated the presence of carboxylic group (—COOH) as well as alcoholic group (—OH) with OH stretching and out of plane deformation motion, respectively. The peaks for the double (C = C) were analyzed in a narrow range of wavenumber between 1620 and 1680 cm^{-1}. Nitro aromatic compounds were detected in a range of 1485 to 1555 cm^{-1}.

The absorption intensity of the ether linkage (—O—) was measured in the range of 1020–1150 cm^{-1}. The functional group of aromatic compounds were between 710 and 860 cm^{-1}. The absorption bands for halogen groups such as fluorine (—F) and chlorine (—Cl) were 1000–1400 cm^{-1} and 540–760 cm^{-1}, respectively. These wavenumber were ranges have been used to identify functional groups of chemical compounds in previous studies (Baltacıoğlu et al. 2021). The results indicated that there was more loss of phenolic compounds at higher microwave powers and vacuum levels compared to lower ones. This loss of functional compounds was due to the thermal degradation at high microwave power which caused the temperature to rise (Kutlu et al. 2021).

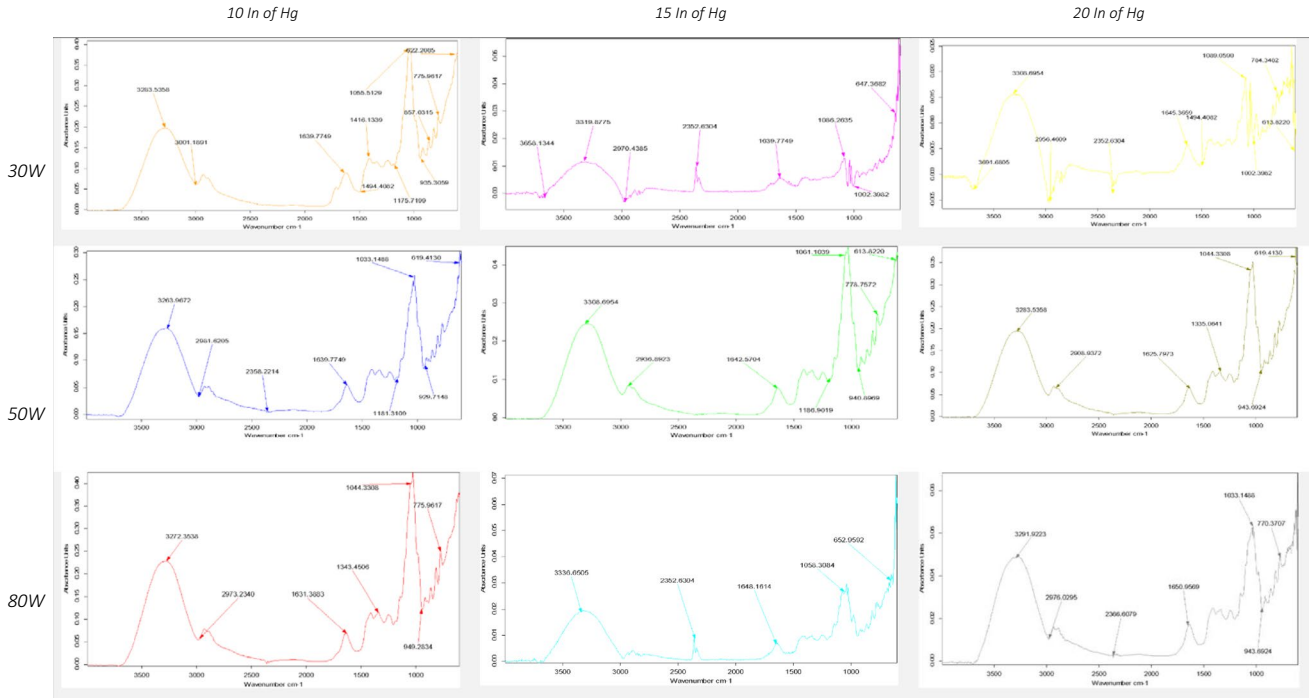

Fig. 4 Effect of microwave power and vacuum pressure on functinal compounds in grape pomace extract

Table 4 Identification of functional groups in grape pomace extract treated under various microwave powers and vacuum levels

Treatments		Wave number (cm^{-1})	Functional group	Vibrational mode
Power (W)	Vacuum (In of Hg)			
30	10	3283.54	- OH, polymer	OH stretching
		3001.19	- OH	OH stretching
		1639.77	C = C	C = C stretching
		1494.41	- NO_2	NO_2 stretching
		1055.51	- O -	R—O stretching
		935.305	- COOH	OH out of plane deformation
		857.03	Ar—H	CH out of plane deformation
		775.96	Ar—H	CH out of plane deformation
		622.21	- Cl	C—Cl stretching
	15	3319.88	≡ C—H	CH stretching
		2970.44	- CH_3	Asymmetric stretching
		1639.77	C = C	C = C stretching
		1086.26	- O -	C—O stretching
		1002.40	- F	C—F stretching
		647.37	- Cl	C—Cl stretching
	20	3308.70	- OH, polymer	OH stretching
		2936.89	- OH	OH stretching
		1642.57	C = C	C = C stretching
		1186.90	- COO -	C—O stretching
		1061.10	- O -	R—O stretching
		940.90	- COOH	OH out of plane deformation
		778.76	Ar—H	CH out of plane deformation
		613.82	- Cl	C—Cl stretching
50	10	3263.97	- OH, polymer	OH stretching
		2981.62	- OH	OH stretching
		1639.77	C = C	C = C stretching
		1181.31	- COO -	C—O stretching
		1033.15	- O -	R—O stretching
		929.71	- COOH	OH out of plane deformation
		619.41	- Cl	C—Cl stretching
	15	3308.70	- OH, polymer	OH stretching
		2956.46	- CH_3	Asymmetric stretching
		1645.36	C = C	C = C stretching
		1494.41	- NO_2	NO_2 stretching
		1089.06	- O -	C—O stretching
		1002.40	- F	C—F stretching
		784.35	Ar—H	CH out of plane deformation
		613.82	- Cl	C—Cl stretching
	20	3283.54	- OH, polymer	OH stretching
		2908.94	- OH	OH stretching
		1625.80	C = C	C = C stretching
		1335.06	- OH	OH in plane deformation
		1044.33	- O -	R—O stretching
		943.69	- COOH	OH out of plane deformation
		619.41	- Cl	C—Cl stretching

Table 4 (continued)

Treatments		Wave number (cm^{-1})	Functional group	Vibrational mode
Power (W)	Vacuum (In of Hg)			
80	10	3272.35	- OH, polymer	OH stretching
		2973.23	- OH	OH stretching
		1631.39	C = C	C = C stretching
		1343.45	- OH	OH in plane deformation
		1044.33	- O -	R—O stretching
		949.28	- COOH	OH out of plane deformation
		775.96	Ar—H	CH out of plane deformation
	15	3336.65	- OH, polymer	OH stretching
		1648.16	C = C	C = C stretching
		1058.31	- O -	R—O stretching
		652.96	- Cl	C—Cl stretching
	20	3291.92	- OH, polymer	OH stretching
		2976.03	- OH	OH stretching
		1650.96	C = C	C = C stretching
		1033.15	- O -	R—O stretching
		943.69	- COOH	OH out of plane deformation
		770.37	Ar—H	CH out of plane deformation

Encapsulation Efficiency

The recovered vapors were encapsulated in sodium alginate microbeads. Encapsulation of bioactive extract was aimed to entrap phenolic compounds for drug delivery applications. Experimental results revealed an encapsulation efficiency of $64 \pm 2\%$, which was in agreement with the results of Moschona and Liakopoulou-Kyriakides (2018) who encapsulated the extract of wine waste of grape white lees, white mac, and red mark chitosan alginate beads and reported encapsulation efficiencies of 55, 77, and 79%, respectively. The higher efficiency of encapsulation indicated that encapsulate had potential for targeted delivery with a solvent free and cleanable extraction process.

Extraction Yield

The extraction efficiency, expressed as a percentage, is the ratio of the amount of moisture recovered (g) during the drying process to the total amount of moisture (g) present in the grape pomace (Fig. 5a). The vapor extraction efficiency was 38.72% at 30 W and 42.58% at 50 W at 10 inHg, respectively. Moreover, the experimental results revealed that the highest power (80 W) produced a maximum value of extraction yield (64.1%). The variation in yield may be attributed to the amount of heat provided by these microwave powers. As discussed earlier, the highest power resulted in maximum moisture removal from the pomace. Thus, maximum amount of vapors was condensed at 80 W.

Likewise, an increasing trend for yield was observed with increasing vacuum level (Fig. 5a). At a constant power of 30 W, increasing the vacuum resulted in 36.88% more moisture recovery from the pomace. This increase was low (10%) at 80 W with the increase in vacuum from 10 inHg to 20 inHg. However, the maximum recovery (70.51%) was observed at 80 W and 20 inHg. This might be due to the high power resulting in rapid removal of moisture from the pomace. Combined effect of pressure was significantly pronounced in this case. At the highest power and vacuum level, i.e., 80 W and 20 inHg, the extract yield was 33.04% higher than 30 W and 20 inHg of processing conditions.

Effective Diffusivity

The effect of different power and pressure levels on effective diffusivity (ED) during the drying of grape pomace

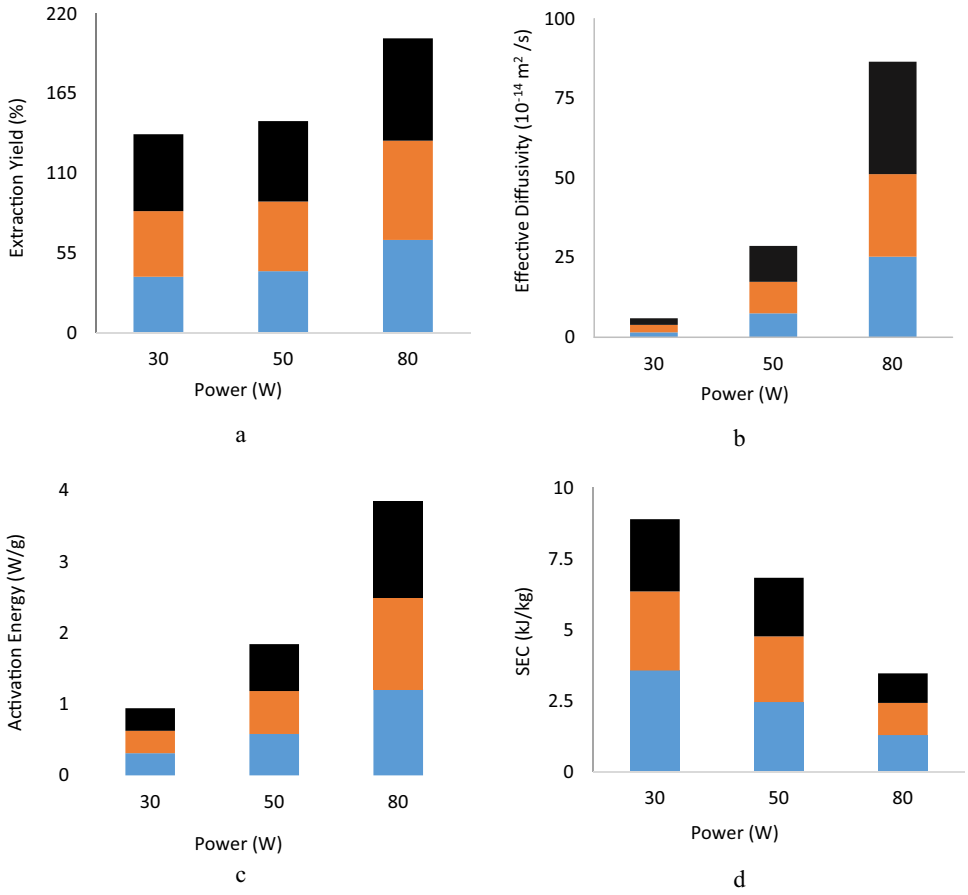

Fig. 5 Effect of different power and vacuum levels (■ 10 inHg, ■ 15 inHg, and ■ 20 in of Hg) on extraction yield (**a**), effective diffusivity (**b**), activation energy (**c**), and specific energy consumption (**d**)

had been drawn in Fig. 5b. It was observed that increase in power levels increased the diffusivity of moisture through the sample. ED value remained same, i.e., 2.43×10^{-7} for all vacuum levels at power of 30 W. However, ED value increased ~ 4 times with the increase in power from 30 to 50 W. This increase was even more pronounced at 80 W, i.e., 8.5, and 2 times compared to 30 and 50 W, respectively. Unlikely, effect of vacuum on ED was non-significant compared to power values; a slight increase in effective diffusivity was observed at 50 and 80 W. While no change in ED was observed at 30 W, similar results were reported by Raj and Dash (2020) who used microwave power and pressure for drying of dragon fruit slice.

Activation Energy

The effect of power and vacuum levels on the activation energy (E_a) of vapor molecules was analyzed (Fig. 5c). Increasing the power level caused an increase in activation energy of the product. For instance, the activation energy increased form 0.12 to 1.44 W/g as the power was increased from 30 to 80 W. This is a 12 time increase that can be attributed to the fact that high temperature produced at high power had rapidly excited the water molecules and caused them to leave the surface. Thus, activation energy during the drying process was increase for all power levels at constant pressure.

The vacuum also influenced an increase in activation energy of the product. An estimated 20% increase was observed when the pressure was increased from 10 to 15 in Hg at constant power (80 W), resulting in a rapid loss of product moisture. This was due to rapid suction of vapors produced by the vacuum, which produced moisture gradient and increased the activation energy requirement of the samples. A further increase in pressure did not significantly influence E_a values. Thus, power had a more significant effect on E_a values than pressure.

Specific Energy Consumption

Specific energy consumption (SEC) was measured as the energy consumption per kilogram of product during drying (Fig. 5d). Increasing the microwave power from 30 to 80 W maximally reduced the value of effective energy consumption from 3.57 to 1.3 kJ/kg, respectively, while keeping the vacuum constant (10 inHg). This represents a 63.58% reduction when the power was increased from 30 to 80 W at

constant vacuum of 10 inHg. However, the lowest values of SEC were observed at 80 W for all pressure levels (1.3, 1.13, and 1.04 kJ/kg at 10, 15, and 20 inHg vacuum, respectively). This decrease may be attributed to the fact that the high microwave powers enhanced the excitation energy of the water molecules in the product to leave the product surface.

The effect of vacuum was also significant in reducing the SEC for pomace drying ($P < 0.05$). At constant power of 30 W, 28.8% reduction in SEC was observed when the vacuum was increased from 10 to 20 inHg. This was the maximum reduction in SEC contents in response to increasing negative pressure at constant power, which was less pronounced with increasing power and vacuum. However, the minimum SEC contents were observed at 20 inHg for all power levels (at 2.54, 2.06, and 1.04 kJ/kg at 30, 50, and 80 W power, respectively). These factors, in fact, reduced the drying time for the high vacuum-power combination, resulting in less energy consumption during the drying. Hence, a combination of high vacuum and power levels is recommended to save time, capital, and energy during the process (Fig. 5).

Conclusion

In the current study, microwave-vacuum-assisted drying was optimized for the drying of grape pomace as well as for the recovery of bioactive compounds. The combined effect of power and vacuum (80 W and 20 inHg) resulted in the highest value of drying rate 5.53 g/100 g min within 10 min of drying process. In addition, it rapidly reduced the moisture ratio, which reduced the processing time. Besides, the effective diffusion and activation energy were significantly influenced by power compared to vacuum levels. Furthermore, the total phenolic contents were not influenced by microwaves and the dried pomace contained more bioactive compounds than the extract (recovered vapors). The results indicated that microwave-vacuum extraction can be used as an environmentally friendly and clean label extraction technique.

Author Contribution A. H.: conceptualization, methodology, investigation, validation, formal analysis, writing—original draft preparation; A. A. M.: methodology, investigation, validation, formal analysis, contribution in writing; M. K. I. K.: methodology, investigation, validation, formal analysis, and contribution in writing in relevant section; A. N.: data analysis, writing—review and editing, final draft supervision and monitoring. M. U. K.: review and editing, final draft supervision and monitoring; M. A. S.: review and editing, final draft supervision, and monitoring; M. R.: review and editing, final draft supervision, and monitoring; J. M. L.: review and editing, final draft supervision, and monitoring. All authors read and approved the final manuscript.

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Data Availability All the data used in the manuscript are available in the tables and figures.

Code Availability Not applicable.

Declarations

Competing interests The authors declare no competing interests.

Ethics Approval Not applicable.

Consent to Participate All authors has given their full consent to participate.

Consent for Publication All authors has given their full consent for publication.

Conflict of Interest Abdul Hameed declares that he no conflict of interest. Abid Aslam Maan declares that he no conflict of interest. Akmal Nazir declares that he no conflict of interest. Usman Amin declares that he no conflict of interest. Muhammad Kashif Iqbal Khan declares that he no conflict of interest. Muhammad Usman Khan declares that he no conflict of interest. Mohammad Ali Shariati declares that he no conflict of interest. Maksim Rebezov declares that he no conflict of interest. José M. Lorenzo declares that he no conflict of interest.

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