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Synergistic effect of microwave heating and hydrothermal treatment on cyanogenic glycosides and bioactive compounds of plum (*Prunus domestica L.)* kernels: An analytical approach

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ABSTRACT

The effects of microwave heating (450 W for 6 min), hydrothermal treatment (6, 9, and 12 h at 45 °C) and their combination on compositional characteristics, cyanogenic glycosides, color, and bioactive compounds of plum kernels have been studied. The conditions examined caused a significant reduction of 37.81, 72.17, 84.41, 91.24 and 98.02% in cyanogenic glycosides of differently treated plum kernels. Total phenolic and total flavonoid compounds of plum kernels showed hydrothermal time-dependent duration decline. The larger shifts in FT-IR spectra near 1157 cm^{-1} provided valuable insights on the reduction of cyanogenic glycosides during combined treatments. The variation of color attributes (L^*, a^*, b^*), during combined treatments indicates a more reddish tonality of plum kernel samples. The combined effect of hydrothermal (12 h at 45 °C) and microwave heating (450 W for 6 min) proved to be an effective tool for neutralizing the toxic effect of cyanogenic glycosides, opening up possibilities for its use in food industries.

1. Introduction

Food processing industries generate a huge quantity of waste products which cause a detrimental environmental effect (Torres-León et al., 2018). Sustainable utilization of agro-food industry wastes for the formulation of novel foods provides an opportunity to reduce environmental pollution in an ecologically safe and economically efficient method (Mohammadi-Moghaddam and Firoozzare, 2021). Plums are mostly consumed as fresh or processed into different value-added products, such as jam, jellies, nectars, dry fruits, etc. (Gornas et al., 2017). During plum processing, tonnes of plum kernels arise as a by-product that is mostly thrown away into the environment or sent to landfills or incinerated, resulting in accumulation in the environment and interfering with the natural process of the ecosystem (Mohammadi-Moghaddam and Firoozzare, 2021). Plum kernels are of paramount importance due to the presence of sufficient quantities of essential oils (32–49.5%) (Kostic et al., 2016), dietary proteins (35–38.1%) (González-García et al., 2016), micronutrients, and bioactive compounds that are mostly underused and undervalued (Savic et al., 2016). The plum kernels are a promising feedstock for oils and proteins due to the high percentage of unsaturated fatty acids (Kiralan et al., 2018), tocopherols (Gornas et al., 2017), and bioactive peptides (González-García et al., 2016). Bolarinwa et al. (2014) reported that plum kernels are cheap sources of bioactive peptides that could be useful for food, cosmetic, and pharmaceutical industries. Nevertheless, the presence of cyanogenic glycosides particularly amygdalin in plum kernels limits its utilization and commercialization for human consumption (Zhang et al., 2019). Cyanogenic glycosides are water-soluble, heat-stable natural plant toxicants that upon hydrolysis produce hydrogen cyanide: a potent respiratory inhibitor (Tanwar et al., 2018). They are widely distributed among the species of the plant kingdom, responsible for bitterness, and develop a characteristic cyanide aroma with moisture (Lee et al., 2013). Consumption of cyanogenic foods has been reported to cause acute and sub-acute health problems in humans such as headache, nausea, vomiting, abdominal cramps, dizziness, weakness, respiratory failures, and death in some extreme cases (Bolarinwa et al., 2014).

To prevent cyanide toxicity, the removal of cyanogenic glycosides has become an indispensable operation unit in the processing of plum kernels (Sheikh et al., 2021a). The conventional methods of peeling, crushing, grinding, soaking, grating, and drying have been used for centuries to remove cyanogenic glycosides of plant foods. Saka and

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Nyirenda (2012) reported that the soaking (48 h) of peeled and unpeeled cassava roots is effective in reducing the cyanogenic glycosides by 97.9%. El-Adawy and El-Kadousy (1995) reported that soaking (1:10) treatment of peach kernels at 47 °C for 30 h caused a marked reduction of 99% in cyanogenic glycoside content. Currently employed conventional detoxification methods are relatively ineffective due to high energy consumption, time waste, labor-intensive, and high loss of nutritive compounds (Saka and Nyirenda, 2012). Recently, great attention has been paid to exploring some novel and green detoxification methods that are relatively low-cost, eco-friendly, and rapid. Microwave heating has been regarded as an alternative to conventional detoxification methods and is regarded as the most promising technique to reduce cyanogenic glycosides (Ivanov et al., 2012). It modifies the nutritional profile by improving the digestibility, producing more desirable flavor compounds while maintaining the equivalent external color levels (Wani et al., 2016). Since in most of the previous studies about the cyanide toxicity of plum kernels, the impact of the combined effect of microwave heating and hydrothermal treatment on cyanogenic glycosides of plum kernels has never been performed. Therefore, to contribute to environmental sustainability and the paucity of data regarding the impact of microwave heating combined with hydrothermal treatment on nutritional and anti-nutritional (cyanogenic glycosides) quality of plum kernels encouraged this investigation.

2. Materials and methods

2.1. Materials and chemicals

The stones from fully matured plum pits used in this work were obtained from Srinagar, Jammu, and Kashmir, India. Pits were decorticated manually to obtain the edible part kernels. The kernels were stored in air-tight zip pouches at 4 °C till further analysis. Amygdalin (>99.0%) and all other chemicals and reagents (analytical or HPLC grades) for the analysis were purchased from Hi-media, Mumbai, India.

2.2. Methods

2.2.1. Hydrothermal treatment

Plum kernels were ground into grits in a grinder (SUJATA, DI/QC/M/2632) and were sieved through B.S.S 6 (410/1969). They were hydrothermally treated in distilled water (1:10 ratio) for 6, 9, and 12 h at 45 °C in a water bath (Model No. NSW-133 (BSS-2), Narang scientific works Pvt. Ltd. New Delhi, India). The method for detoxification of plum kernels grits was adapted from Sheikh et al. (2021b). Soaked grits were taken out of the water and dried in a tray drier at 40 ± 2 °C for 6 h. Samples were finely ground, vacuum packed, and kept in low-density polyethylene (LDPE) pouches under freezing conditions till further analysis.

2.2.2. Microwave heat-treatment of plum kernel flour

A microwave oven (Samsung, MS23K3513AK/T) able to generate 900 W energy at 2450 MHz was used for heating experiments. Microwave output energy was estimated as stated by Juhaimi et al. (2018). 100 g raw and hydrothermally (6, 9 & 12 h) treated plum kernels were spread on 16 cm Petri-plate in a thin layer and positioned on a vorticular platter of the microwave oven, and heated at 450 W for 6 min. The differently treated samples were cooled in a desiccator and stored in zip pouches at 4 °C till further investigation. An untreated sample was used as a control.

2.2.3. Chemical composition

Chemical characteristics like moisture, crude oil, crude protein, crude fiber, and total ash were determined by following the standard protocols 950.01, 920.39, 945.01, 985.29, and 942.05, respectively, (AOAC, 2000). All of the analyses were executed in triplicate and final results are presented as their means.

2.2.4. Extraction of phenolic compounds from plum kernel flour

Phenolic compounds of plum kernel flour were extracted according to Lin et al. (2016). About 5 g of defatted residue was extracted in 50 mL with methanol/water solution (20:80 v/v) in an ultrasonic water-bath at 40 °C for 60 min, followed by extraction under reflux condition for 2 h. After centrifugation (Model NO. RC 8100 SFS, Elektrocraft India Pvt. Ltd. Mumbai) at 6000 g × 10 min, the supernatant was filtered (Whatman filter paper 42, ashless, diameter 125 mm, 100 circles). The filtrates were evaporated under vacuum, followed by lyophilization to obtain the methanolic extract, re-dissolved in methanol (50 mg/mL), and kept at 4 °C till further investigation.

2.2.4.1. Total phenolic content (TPC) of plum kernel flour. The total phenolic compound content in extracts was determined using the Folin-ciocalteu colorimetric method as described by Lin et al. (2016). Extract (50 μL) was added to 1 mL of distilled water and 0.5 mL of Folin-Ciocalteu reagent. After 3 min 2.5 mL of 10% sodium carbonate was added and samples were kept in dark at room temperature for 20 min. The absorbance against control was recorded at 735 nm (S2100UV + Spectrophotometer, Model No. UV2100PU, United Products & Instruments Inc.). Gallic acid was used to as a standard to produce a calibration curve, and the results were presented as mg gallic acid equivalents (GAE) per g of sample.

2.2.4.2. Total flavonoid content (TFC) of plum kernel flour. The flavonoid levels of the extracts were assessed by using aluminium chloride colorimetric method as described by Lin et al. (2016). An aliquot (250 μL) was added to 1.25 mL of distilled water and 75 μL of 5% sodium nitrate. After 6 min, 150 μL of 10% $AlCl_3$ was introduced to the solution accompanied by a reaction for 5 min. Afterward, 0.5 mL of 1 M NaOH solution and 275 μL of ethanol were supplemented to the solution, and the reaction mixture absorbance was recorded immediately against control at 510 nm (S2100UV + Spectrophotometer, Model No. UV2100PU, United Products & Instruments Inc.). Catechin standard solution was used for the calibration curve and the flavonoid content was present as mg catechin equivalent (CE) per g of extract.

2.2.5. Determination of cyanogenic glycosides

Total cyanogenic glycosides of plum kernels samples were evaluated using the procedure reported by Ezeonu and Ejikeme (2016). 1 g of plum kernel sample was added to 200 mL of distilled water in a round bottom flask and allowed to stand for 2 h for autolysis. 0.5 g of tannic acid (antifoaming agent) was added to the round bottom flask followed by distillation. The distillate was collected in a 250 mL conical flask containing 20 mL of 2.5% of sodium hydroxide. To 100 mL of distillate, 8 mL of ammonium hydroxide and 2 mL of potassium iodide were added. The solution was mixed and titrated with 0.02 M silver nitrate against a blank sample. Cyanogenic glycoside content of the plum kernel samples was calculated as:

$$\text{Cyanogenic glycosides}\left(\frac{\text{mg}}{100\ \text{g}}\right)=\frac{\text{Titre Value}\times 1.08\times\text{Exact volume}}{\text{Aliquot Volume}\times\text{weight of sample (g)}}\times 100 \quad (1)$$

2.2.6. Color characteristics

The color characteristics of both raw and microwave treated samples were evaluated by using the CIELAB-indices. The glass cell holding the sample was placed above the light source of the Hunter colorimeter (Color i5, Gretag Macbeth) in reflectance mode. The color attributes L^*, a^*, and b^* of ten replicates of both raw and treated samples were recorded, where L^* displays the lightness, $\pm a^*$ displays reddish to a greenish color, and $\pm b^*$ displays bluish to yellowish color of the sample. The colorimetric difference (ΔE^*), chroma (C*), hue angle (Ha), browning index (BI), and total color (E^*) of both raw and microwave treated samples were used to calculate from colorimetric parameters according to the respective equations as follows:

$$\Delta E^* = \sqrt{((L^* - Lo)^2 + (a^* - ao)^2 + (b^* - bo))^2} \quad (2)$$

where.

L_o, a_o and b_o represents the colorimetric parameters of the control sample

$$C^* = \sqrt{(a^*)^2 + (b^*)^2} \quad (3)$$

$$Ha = \tan^{-1}\left\{\frac{a^*}{b^*}\right\} \quad (4)$$

$$BI = 100 \times \frac{X - 0.31}{0.17} \quad (5)$$

where,

$$X = \frac{a^* + 1.75 \times L^*}{5.645 \times L^* + a^* - 3.12 \times b^*}$$

$$E^* = \sqrt{(L^*)^2 + (a^*)^2 + (b^*)^2} \quad (6)$$

2.2.7. Fourier transform infrared (FTIR) analysis

The samples were ground and the flour was applied onto a potassium bromate disk to form a thin layer. The absorption spectra of all plum samples were recorded from 400 to 4000 cm^{-1} at a resolution of 2 cm^{-1}.

2.2.8. Statistical analysis

The results are expressed as a mean of three observations ± standard deviation. Statistical analysis was performed using a one-way analysis of variance (ANOVA) at a significance level of 5%. Significant differences among different samples were estimated using DUNCAN'S multiple range test (STATISTICA7.ink).

3. Results and discussion

3.1. Composition of plum kernel flour obtained from different microwave and hydrothermal treatments

For the effect of treatments on the moisture content, microwave heating for 6 min (A1) induced the highest reduction of 37.17%, while the combined effect of microwave and hydrothermal treatments (A3, A4, and A4) led to a reduction of 13.71, 9.14, and 3.97% respectively, when compared with that of the native (N) sample (Table 1). On the contrary, an increment of 27.63% in moisture content was recorded for the sample soaked at 45 °C for 10 h (A2). The reduction of moisture content in the combined treatment of soaking and microwave (A3, A4, and A5) might be attributed to the evaporation of intercellular water due to volumetric heat generation by microwave radiation (Lenaerts et al., 2018). The reduction in moisture content is accelerated due to the absorption of microwave energy by the water molecules, as a consequence, internal vapor pressure generation leads to the development of a pressure gradient which significantly increases the rate of moisture migration from inside to outside of the sample (Fazaeli et al., 2012). The

Table 1
Effect of microwave, hydrothermal and their combined treatments on the compositional characteristics of the plum kernels.

Sample	Moisture content (%)	Protein content (%)	Crude fat (%)	Crude fiber (%)	Total ash (%)	Carbohydrates (%)
N	5.03 ± 0.12^{d}	35.24 ± 0.27^{a}	46.04 ± 0.69^{b}	2.70 ± 0.11^{d}	2.59 ± 0.04^{d}	8.31 ± 0.23^{b}
A1	3.16 ± 0.11^{f}	34.65 ± 0.13^{b}	47.18 ± 0.18^{a}	2.71 ± 0.09^{e}	2.72 ± 0.02^{e}	8.21 ± 0.31^{a}
A2	6.42 ± 0.21^{a}	33.87 ± 0.35^{d}	45.24 ± 0.31^{d}	3.08 ± 0.07^{c}	2.43 ± 0.03^{d}	7.43 ± 0.11^{e}
A3	4.34 ± 0.09^{c}	34.16 ± 0.23^{c}	45.41 ± 0.25^{b}	3.16 ± 0.09^{b}	2.62 ± 0.02^{c}	7.96 ± 0.16^{c}
A4	4.57 ± 0.14^{b}	33.51 ± 0.16^{e}	45.20 ± 0.13^{c}	3.62 ± 0.12^{a}	2.28 ± 0.01^{b}	7.68 ± 0.13^{d}
A5	4.83 ± 0.10^{b}	33.09 ± 0.11^{f}	45.14 ± 0.10^{e}	4.16 ± 0.15^{a}	2.16 ± 0.08^{a}	7.19 ± 0.12^{f}

N: Native plum kernel sample; A1: Plum kernel sample microwaved at 450 W for 6 min; A2: Plum kernel sample soaked for 9 h at 45 °C; A3: Plum kernel sample soaked for 6 h at 45 °C and microwaved at 450 W for 6 min; A4: Plum kernel sample soaked for 9 h at 45 °C and microwaved at 450 W for 6 min and A5: Plum kernel sample soaked for 12 h at 45 °C and microwaved at 450 W for 6 min.

increased moisture content in A2 was reported to be due to a greater imbibement of water by the plum kernel samples during hydrothermal treatment. The protein content decreased during the treatments, with the highest protein reduction of 6.10% estimated in A5, while the lowest (1.67%) was observed in A1. Lenaerts et al. (2018) reported that the decrease in crude protein values during heating may be due to the coagulation of protein denaturation, while the reduction in A2, may be attributed to the leaching of soluble proteins into the soaking medium and microwave heating adds an aspect to thermal degradation due to dismantling of the cell-matrix during the combined soaking and microwave (A3, A4, and A5) treatments. The crude oil content of A1 was found to be higher than that of a native as well as of other treated samples. The lower oil yield of the native sample was due to the intactness of the cell wall during extraction. After microwaving, oily cells are ruptured and the increase in porosity facilitates the easy flow of oils (Fathi-Achachlouei et al., 2019). The low extraction yield of the crude oil in A2, A3, A4, and A5 is related to a high moisture content of the samples due to the diffusion of water between the capillaries and inter-cellular spaces during hydrothermal treatments. Romero-Guzmána et al. (2020) reported that the reduction in oil content might be due to interference in fat analysis which could result from the formation of the fat-protein complex during hydrothermal treatments. The highest yield of crude fiber was found in A5, while the lowest in the native sample. The fluctuations in crude fiber and total ash contents might be related to the decrease in other macronutrients of the plum kernel samples during the treatments. The highest reduction in carbohydrate was observed in A5, which might be attributed to the higher water solubility of carbohydrates due to the breakdown of complex constituents during hydrothermal treatments, which results in greater leaching of soluble compounds into the soaking medium.

3.2. Effect on total phenolic content (TPC)

The consumption of phenolic compounds has been associated with health benefits such as the prevention of several chronic degenerative diseases and slowing the aging process. These effects are related to the antioxidant potential of the phenolic compounds present in the fruit and vegetables. Generally, food-processing techniques are recognized as one

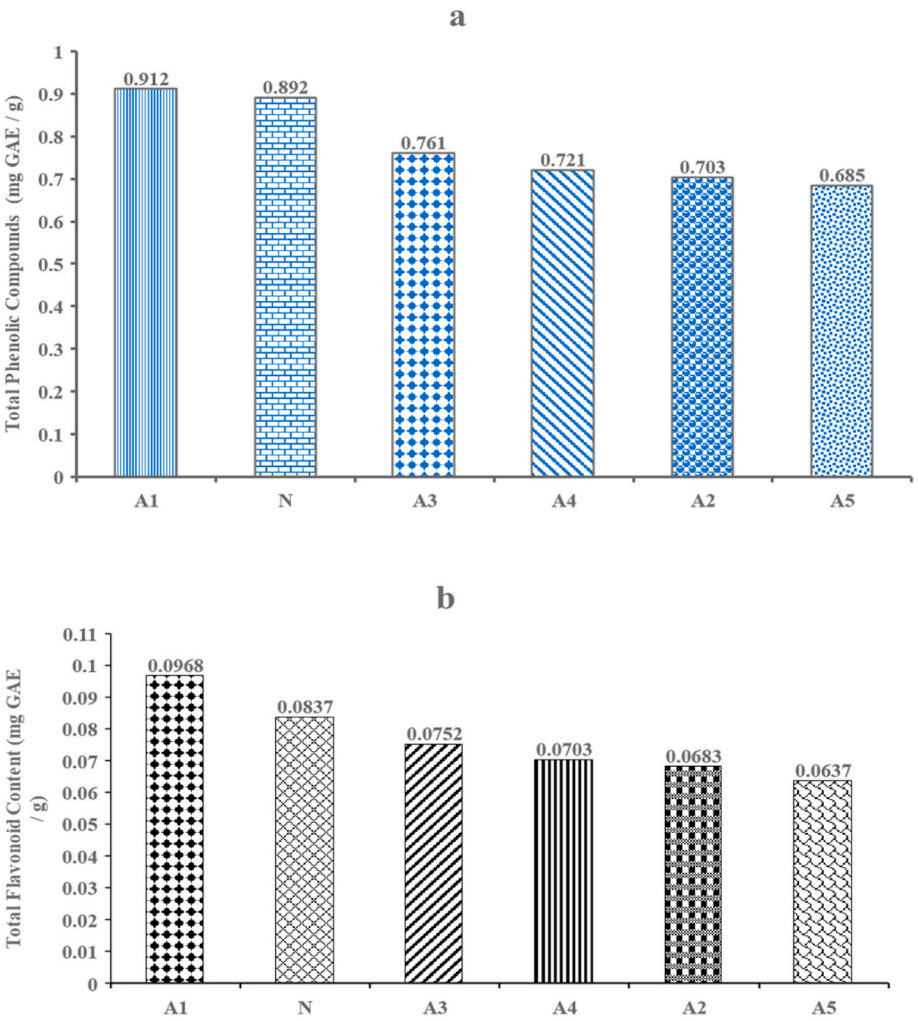

Fig. 1. (a) Total phenolic compounds (TPC) and **(b)** total flavonoid compounds (TFC) of N: Native plum kernel sample; A1: Plum kernel sample microwaved at 450 W for 6 min; A2: Plum kernel sample soaked for 9 h at 45 °C; A3: Plum kernel sample soaked for 6 h at 45 °C and microwaved at 450 W for 6 min; A4: Plum kernel sample soaked for 9 h at 45 °C and microwaved at 450 W for 6 min and A5: Plum kernel sample soaked for 12 h at 45 °C and microwaved at 450 W for 6 min.

of the major factors in the destruction of natural phytochemicals, which may affect the antioxidant capacity in foods. The TPC of the plum kernel samples obtained at different hydrothermal, microwave, and combined treatments exhibited significant ($p < 0.05$) variations (Fig. 1a). The increased content of phenolics in plum kernel samples which were only microwaved (A1) may have been the consequence of high temperature, water stress, breakdown of cellular constituents and lignocellulosic structures, and partly accounted for the formation of Maillard reactions products, which are formed at higher temperatures and lead to an appreciable bioavailability of the phenolic compounds by liberating them from the plant matrix (Wani et al., 2016). The observed reduction of TPC in samples that were soaked only (A2) could be attributed to leaching out of soluble phenolic compounds in the soaking medium. The increase in cell membrane permeability during hydrothermal treatment of plum kernels facilitates polyphenolic reduction due to the penetration of solvent in the plant matrix (Nayak et al., 2015). The extraction yield of phenolic compounds is significantly dependent on the structural and compositional characteristics of the plant matrix and the bond with which they are bound to the matrix (Zuorro et al., 2019). Plant cells are poorly permeable to the solvent, but their compactness can be reduced by the disruption of solute-matrix interactions due to the absorption of solvent molecules. Hydrothermal treatment opens up the cell-matrix and thereby increases the polyphenols migration into the soaking medium (Nayak et al., 2015). At the same time, combined treatments of soaking and microwave (A3, A4, and A5) also showed a considerable reduction in TPC because the hydrothermal treatment promotes the breakage of phenolic interactions with other organic substances such as proteins or carbohydrates, and microwave heating induces the hydrolysis of conjugated phenolic compounds, allowing unbound phenolic compounds to solubilize and diffuse into the soaking medium (Mecha et al., 2019).

3.3. *Effect on total flavonoid content (TFC)*

Flavonoids represent the most common and widely distributed group of phenolic compounds in fruits and vegetables. The regular intake of flavonoids is associated with a reduced risk of cardiovascular diseases and an overall improvement in health. They are the most common pigments, next to chlorophyll and carotenoids responsible for most of the yellow, red, and blue colors in the plant kingdom. The slight increase in the measured TFC content in plum kernels samples which were only microwaved (A1) might be due to the de-structuration of matrix linked to the flavonoid substances, which resulted in a greater release of bound flavonoids when a higher temperature is applied (Fig. 1b). The obtained results were in agreement with the results of Juhaimi et al. (2018), who reported that the optimum microwave roasting power of apricot kernels from the standpoint of bioactive compounds is 540 W. On the contrary, the observed reduction of TFC in plum kernels samples which were soaked only (A2) and plum kernels samples were given the combined treatment of soaking and microwave (A3, A4, and A5) was attributed to the longer soaking duration, allowing unbound phenolics to solubilize

and diffuse into the soaking medium. It has been reported that the thermal conditions might result in the loss of flavonoids and the effect of degradation depends on the thermal conditions and the number of hydroxyl and methoxyl groups of flavonoids (Nayak et al., 2015). The reduction of flavonoid content could be attributed to structural modification or the degradation of naturally occurring forms of flavonoids during thermal processing. At the same time, the combination of microwave heating with hydrothermal adds an additional aspect of thermal degradation as well as disruption of cell structures that results in more leaching of soluble TFC's into the soaking medium. Kao et al. (2004) reported that the leaching of flavonoids to the soaking medium depends upon a time-temperature combination of the processing method and chemical structure of the flavonoids. Dulf et al. (2016) reported that thermal processing was shown to release more bound phenolic compounds due to the breakdown of cellular constituents.

3.4. Effect on cyanogenic glycosides

Cyanogenic glycosides are water-soluble compounds that are stored in separate compartments in intact cells. The key characteristic of these compounds is the formation of hydrocyanic acid upon the tissue disruption. Depending upon the chemical structure, different cyanogenic compounds release different amounts of hydrogen cyanide, like amygdalin releasing 59 mg HCN/g cyanogenic compound (EFSA CONTAM Panel, 2020). The results revealed that the application of microwave, hydrothermal, and their combined treatments had a significant ($p < 0.05$) effect on the reduction of cyanogenic glycosides of plum kernel samples (Fig. 2). The percentage reduction of 37.81, 72.17, 84.41, 91.24, and 98.02% in the content of cyanogenic glycosides was observed during A1, A2, A3 A4, and A5 treatments of plum kernel samples, respectively. The reduction of cyanogenic glycosides during microwave treatment (A2) could be attributed to acute heat stress caused by non-ionizing radiation which destroys the liberated hydrogen cyanide by volatilization (Vijayakumari et al., 2007). The levels of cyanogenic glycosides of presently investigated native and differently treated plum kernel samples showed a time-dependent decline when combined treatment of microwave at 450 W for 6 min and soaking at 45 °C for 6, 9, and 12 h was applied. The hydrocyanic acid produced during hydrolysis of cyanogenic glycosides is water-soluble and this accounts for the reduction of cyanide content during hydrothermal treatment. Similarly, Onwuka (2006) reported that the cyanogenic glycoside content of cowpeas was completely reduced (100%) due to the hydrolysis process of cyanogenic glycosides by prolonging the boiling time to 1 h after soaking for 12 h. Feng et al. (2003) reported that microwave heating at 400 W for 4 min 50 s was ideal to reduce the HCN content below the allowed limits in the flaxseed. The level of cyanogenic glycosides in plum kernel samples (A5) seems to be negligible when compared with the lethal level of hydrocyanic acid (36 mg/100 g). The higher reduction in the level of cyanogenic glycosides during combined treatments (A3, A4, and A5) than A1 and A2 treatments probably resulted from the leaching of increased free forms of cyanogenic glycosides due to the dismantling of cell-matrix by hydrothermal treatment followed by microwave heating at 450 W for 6 min, which adds an additional aspect to thermal degradation of remaining cyanogenic glycoside compounds of plum kernel samples (Kala and Mohan, 2012). The results of the present study demonstrated that the extent of reduction was dependent on the process conditions and the combined treatment of soaking for 12 h at 45 °C and microwave at 450 W for 6 min (A5) reduced the cyanogenic glycosides under the allowed limits as set by European Commission Regulation (EU) (2017/123712) (EFSA CONTAM Panel, 2020).

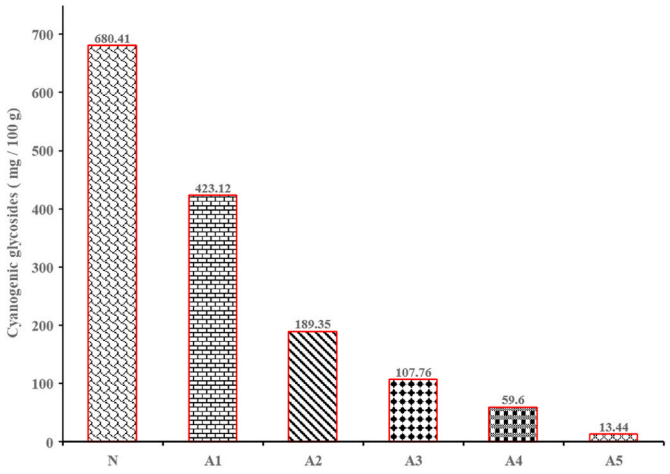

Fig. 2. Cyanogenic glycosides of N: Native plum kernel sample; A1: Plum kernel sample microwaved at 450 W for 6 min; A2: Plum kernel sample soaked for 9 h at 45 °C; A3: Plum kernel sample soaked for 6 h at 45 °C and microwaved at 450 W for 6 min; A4: Plum kernel sample soaked for 9 h at 45 °C and microwaved at 450 W for 6 min and A5: Plum kernel sample soaked for 12 h at 45 °C and microwaved at 450 W for 6 min.

3.5. Effect on color parameters

Color is an important quality parameter for determining the optical acceptance and the commercial value of the product. In comparison to the native sample, the use of microwave, hydrothermal and their combined treatment promoted significant ($p < 0.05$) color changes in plum kernel samples (Table 2). The decreased value of lightness (L^*) in A1, A2, A3, A4, and A5 treated samples might be attributed to leakage or partial solubilization pigments from the cell compartments due to cell rupturing as a consequence of thermal treatments (Nawaz et al., 2018). Our results are in agreement with Zheng et al. (2018), who reported that decreased L^* value is typically more associated with heat processing as it initiates the formation of degradation products called melanoidins that imparts a brown color and subsequently gave the microwaved samples a darker color. A slight variation in 'a^*' (green-red coordinate) and 'b^*' (blue-yellow coordinate) values was observed among differently treated plum kernel samples, which indicates an increase in the redness ($+a^*$) and yellowness ($+b^*$) of the color. The enhancement in 'a^*' and 'b^*' values might be due to the degradation of phospholipids as well as pigments during the heating process (Zheng et al., 2018). The total color change (ΔE) of plum kernels samples varied significantly ($p < 0.05$) during hydrothermal and microwave treatments. ΔE indicates the magnitude of color difference between samples or the human ability to differentiate among colors of the sample and plays a significant role in evaluating color accuracy. A marked change in the ΔE value of the sample with combined treatment of soaking for 12 h at 45 °C and microwaved at 450 W for 6 min (A5) was likely related to a high change in the L^* and b^* values due to the solubilization of pigments or degradation of polyphenols or the formation of Maillard reaction products because of thermal effects. Moreover, a significant variation in chroma (C) and hue (Ha) values of plum kernel samples were noticed during the treatments. Chroma is an indicator of the color intensity perceived by the human vision and represents the stability of color, while hue refers to the product tonality or pure color and defines the basic coloring of the sample. The decrease of C values of plum kernel samples during microwave and hydrothermal treatments indicates that its coloration changed towards pure grey. Hue is considered as a qualitative quality of the color which is traditionally based on reddish, greenish, and others. The decrease in Ha during different treatments (A1, A2, A3, A4, and A5) indicates more reddish tonality (Malik et al., 2021). To evaluate the overall color change more precisely, browning indices (BI) were calculated, which represent the purity of brown coloring. The greater reduction in L^* value due to the higher concentration of brown pigments could be attributed to the increase in BI. The variation of total color as a function of color attributes (L^*, a^*, b^*), indicates an improvement of color during microwave and hydrothermal treatments as a result of the

Table 2
Effect of microwave, hydrothermal and their combined treatments on the color parameters of plum kernel.

Sample	*L**	*a**	*b**	*ΔE**	Chroma	Hue	*BI*	*E**
N	51.07 ± 0.54^{a}	4.18 ± 0.12^{e}	26.89 ± 0.66^{a}	Nil	27.21 ± 0.18^{a}	1.41 ± 0.04^{a}	77.87 ± 0.25^{e}	57.87 ± 0.39^{a}
A1	47.34 ± 0.33^{b}	8.09 ± 0.32^{b}	24.05 ± 0.39^{c}	6.10 ± 0.09^{d}	25.37 ± 0.23^{c}	1.24 ± 0.02^{c}	81.30 ± 0.18^{d}	53.71 ± 0.54^{b}
A2	46.01 ± 0.29^{c}	7.92 ± 0.29^{b}	23.96 ± 0.14^{c}	6.89 ± 0.11^{c}	25.33 ± 0.16^{c}	1.25 ± 0.03^{bc}	84.18 ± 0.13^{c}	52.52 ± 0.22^{c}
A3	44.94 ± 0.45^{d}	6.46 ± 0.41^{d}	22.9 ± 0.44^{d}	6.85 ± 0.05^{c}	23.79 ± 0.24^{d}	1.29 ± 0.02^{b}	78.03 ± 0.32^{f}	51.74 ± 0.12^{d}
A4	43.04 ± 0.68^{e}	8.80 ± 0.23^{a}	24.98 ± 0.59^{b}	9.45 ± 0.13^{b}	26.48 ± 0.26^{b}	1.23 ± 0.01^{c}	97.97 ± 0.29^{a}	50.54 ± 0.34^{e}
A5	37.09 ± 0.76^{f}	7.17 ± 0.33^{c}	20.08 ± 0.47^{e}	15.83 ± 0.14^{a}	21.32 ± 0.27^{e}	1.22 ± 0.02^{c}	89.32 ± 0.13^{b}	42.78 ± 0.33^{f}

N: Native plum kernel sample; A1: Plum kernel sample microwaved at 450 W for 6 min; A2: Plum kernel sample soaked for 9 h at 45 °C; A3: Plum kernel sample soaked for 6 h at 45 °C and microwaved at 450 W for 6 min; A4: Plum kernel sample soaked for 9 h at 45 °C and microwaved at 450 W for 6 min and A5: Plum kernel sample soaked for 12 h at 45 °C and microwaved at 450 W for 6 min.

interaction of reducing sugars with primary amino acids. The results are in agreement with the trend reported by Zheng et al. (2018), who suggested that the generation and accumulation of Maillard-derived melanoidins (brown pigment) during the roasting process might be responsible for color development. Similar findings were reported by Malik et al. (2021), who suggested that the color change phenomenon appeared due to the formation of polyene and other low and high molecular weight brown pigments during hydrothermal treatment of amaranth.

3.6. FT-IR analysis

FT-IR is an incredibly versatile material analysis technique, a great tool to determine the molecular composition, structure, and chemical identification of the substance hastily and economically. The FT-IR spectra allow an analysis of the samples without their disruption, providing a comprehensive chemical fingerprint of the sample composition. The native and differently treated plum kernel samples offered an identical impression of absorption bands which signifies the resemblance of compounds present in each sample (Fig. 3). The absorption bands (group frequencies) observed above 1500 cm^{-1} signify the presence of specific functional groups like methylene (CH_2), hydroxyl (OH), and carbonyl (C=O) groups, while the absorption bands (fingerprint frequencies) below 1500 cm^{-1} indicate the characteristics of the molecules as a whole. The characteristic absorption bands recorded in the range of 4000 - 2500 cm^{-1} indicates a single bond region like O-H (alcohol), N-H, and C-H (alkane) groups, 2500 - 2000 cm^{-1} the range indicates triple bond regions like C≡C and C≡N groups, 2000 -1500 cm^{-1} indicates C=C, (arene) C=O (ester), and C=N groups, and 1500 - 600 cm^{-1} indicates fingerprint region (Divekar et al., 2017). Due to the applied microwave, hydrothermal, and combined treatments, there were notable differences in spectral intensity among the plum kernel samples. The broad and medium absorption peaks noticed at different wavenumbers indicate a change in the composition and structure of the plum kernel samples during different treatments. The broad absorption bands around 3268.9, 3282, 3270.4, 3272.2, 3281.4 in different plum kernels samples are displayed by O-H bonds, such as those found in alcohols and carboxylic acids, signifying O-H stretching vibrations. The band near 3007.11, 2970.25, 2923.44, and 2853.73 cm^{-1}, signifying the existence of aliphatic C-H, O-H, and N-H bond stretching and bending vibrations of both symmetric as well as asymmetric (Matwijczuk et al., 2019). The shifting of band positions around 3000 cm^{-1} is indicative of lipid phase changes due to microwave heating (Divekar et al., 2017). The other very important vibration regions were noticed at 1743.74 cm^{-1}, which were typical of the stretching vibrations of the carbonyl group in the ester group of acylglycerols (Wani et al., 2016). The decrease in the intensity of the 1743.74 cm^{-1} bands in treated samples is an indication that the carbonyl group contents of differently treated plum kernel samples were reduced. The next absorption bands with a maximum at 1643, 1641, 1651, 1636, 1630, 1633 cm^{-1}, signifying the stretching vibrations of -C=C- group, and the intensity of these bands also decreased with A1, A2, A3, A4, and A5 treatments, respectively. The next important bands at 1546, 1529, 1567, 1542, 1549, and 1539 cm^{-1} are related to various vibrations originating from -C-C- and -C=C- groups and evidencing the aromatic skeletal stretching (Matwijczuk et al., 2019). The bands at 1456, 1429, 1438, 1461, 1443, and 1455 cm^{-1} are the results of CH_2 deformation stretching of aromatic rings (Divekar et al., 2017). The absorption band ~ 1157 cm^{-1} reflects the C-O asymmetric bond stretching vibration of the amygdalin molecule (a cyanogenic glycoside) containing cyclic ether bond. The decrease in the intensity of ~ 1157 cm^{-1} band in treated samples is an indication that the cyanogenic glycoside content of the differently treated plum kernel samples was reduced (Savic et al., 2016). The larger shifts in the FT-IR spectra of plum kernel samples ~ 1157 cm^{-1} with combined treatment of soaking for 12 h at 45 °C and microwaved at 450 W for 6 min (A5), reflected a greater change in the functional groups, such as aromatic and cyano groups of the plum kernel samples. The absorption band observed at ~1019 cm^{-1} reflects the C-C, C-OH, and C-H stretching vibration. The absorption bands ~ 722 cm^{-1} corresponds to the variable angle variation and bending vibration of alcohols containing hydroxyl groups and benzene groups (Matwijczuk et al., 2019). Evidently, by correlating the FT-IR spectra of the native sample with differently treated samples, many differences were observed in the position or intensity of the absorption bands and the effect of the treatment can be distinguished by the shifting of absorption peak towards slightly higher or lower wavelengths, which might be responsible for the structural and chemical changes of the samples. Chavez-Murillo et al. (2018) reported that the use of hydrothermal treatment resulted in the greater unfolding of protein structures, increased the motion range of molecules, and might be a feasible alternative to obtain functional ingredients.

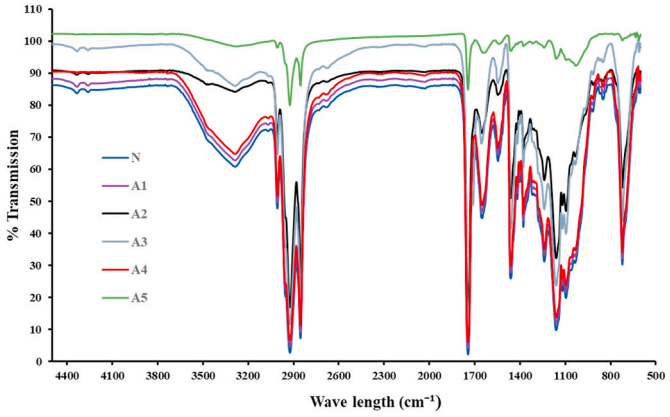

Fig. 3. FT-IR Spectra of N: Native plum kernel sample; A1: Plum kernel sample microwaved at 450 W for 6 min; A2: Plum kernel sample soaked for 9 h at 45 °C; A3: Plum kernel sample soaked for 6 h at 45 °C and microwaved at 450 W for 6 min; A4: Plum kernel sample soaked for 9 h at 45 °C and microwaved at 450 W for 6 min and A5: Plum kernel sample soaked for 12 h at 45 °C and microwaved at 450 W for 6 min.

4. Conclusion

Plum kernels are mostly underutilized and undervalued due to the presence of cyanogenic glycosides. The present work was carried out to investigate the effects of microwave heating (450 W for 6 min), hydrothermal treatment (6, 9, and 12 h at 45 °C), and their combination in eliminating the cyanogenic glycosides from plum kernel sample. Compared to the native sample, all examined conditions caused substantial variations in compositional characteristics, cyanogenic glycosides, total phenolic and total flavonoid compounds of plum kernel samples. Of the attempted detoxification methods, soaking of plum kernel grits at 45 °C for 12 h followed by microwaving at 450 W for 6 min (A5) proved to be most effective in reducing the cyanogenic glycosides to negligible amounts. The results suggested that the A5 treatment could be an effective tool for neutralizing the toxic effect of cyanogenic glycosides and adoption of such cost-effective detoxification techniques may enhance the biological quality of the plum kernel for the production of essential oils, dietary proteins, and bioactive peptides. It is a milder, less laborious process and would be a preferable treatment for the detoxification of plum kernels. This study might probably provide the basis for a sustainable procedure of integrated exploitation of plum kernels and opening up possibilities for its use in food industries. To attain the maximum economical and efficient utilization of such waste products for protein and oil production, more information about the effects of novel non-thermal techniques on the cyanogenic glycosides, antioxidant potential, fatty acid profile, amino acids, and compositional characteristics of plum kernels are required.

CRediT authorship contribution statement

Mohd Aaqib Sheikh: Investigation, Methodology, Formal analysis, Writing – original draft. **Charanjiv Singh Saini:** Resources, Conceptualization, Funding acquisition, Supervision, Writing – review & editing. **Harish Kumar Sharma:** Supervision, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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