

COMPARATIVE ELUCIDATION OF GARLIC PEELING METHODS AND POSITIONING OF QUALITY CHARACTERISTICS USING PRINCIPAL COMPONENT ANALYSIS

Prem Prakash, Kamlesh Prasad✉

Department of Food Engineering and Technology, Sant Longowal Institute of Engineering & Technology
Longowal – 148106, Distt. Sangrur (Pb.), India

ABSTRACT

Background. Garlic (*Allium sativum*) peeling is one of the crucial steps in its use and is a significant challenge for maintaining the peeled garlic's quality. The peeling of garlic on a mass scale is required to produce dehydrated garlic flakes, powder, grits, paste, garlic pickle, and for use as a critical wet spice in various processed products.

Materials and methods. Manual peeling (MP), normal water peeling (NWP), hot water peeling (HWP), flame peeling (FP), and lye peeling (LP) methods were assessed for the quality characteristics of peeled garlic cloves based on antioxidant activities (AOA), total phenolic content (TPC), total flavonoid content (TFC), anti-nutritional properties, ascorbic acid (AA), reducing sugar, allicin, and pyruvic acid content. Principal component analysis (PCA) was used to develop the correlations between the garlic peeling methods and the measured parameters. Morphological and Energy Dispersive X-Ray (EDX) analyses were used to verify the difference between the optimized method of peeled garlic over the manually peeled garlic.

Results. All peeling methods of garlic resulted in the respective peeled garlic having a pH in the acidic range (6.08–6.14). Reducing sugar is an important component affecting the color of the dehydrated garlic, which was found to be minimal in NWP (275.64 mg/g, fresh weight) and LP (335.26 mg/g, fresh weight). Allicin content, pyruvic acid, TPC, TFC, and AOA were similar for manually and lye-peeled garlic. MP garlic had the highest levels of anti-nutritional factors, such as saponin, phytic acid, and tannin. Whereas, the minimum level of saponin was found in HWP garlic. Phytic acid and tannin content were found to be minimum in LP and FP garlic. Multivariate analysis showed that the estimated chemical attributes were found to have the maximum number of positive correlations with the LP methods of garlic. At the same time, it also showed less correlation with anti-nutritional properties and a negative correlation with reducing sugar. Thus, the lye peeling (LP) method may be applied commercially for garlic peeling on a commercial scale due to it maintaining the quality characteristics; the morphological and EDX analyses also support this finding.

Conclusions. LP method was found to be the best method of peeling since it maintained the allicin content, antioxidant properties, and reduced anti-nutritional properties and doesn't reduce sugar.

Keywords: garlic, allium sativum, peeling methods, multivariate analysis, principal component analysis, quality

INTRODUCTION

India contributes approximately 10.4% of the total garlic production in the world (FAOSTAT, 2021). The utilization of garlic at the domestic and industrial scale is limited due to the inherent difficulty in its peeling.

✉ profkprasad@gmail.com, <https://orcid.org/0000-0001-7086-9391>

This limitation could be solved by adopting an appropriate peeling method which preserves the garlic quality. Garlic cloves are arranged in irregular concentric rings around the central floral axis as a compound tunicated bulb and are classed under the category of the modified stem of the allium species. They consist of several fleshy, sickle-shaped scales and are called bulblets or cloves. All tunicated bulbs are joined together by a discoid stem and adventitious root. The fleshy part of an individual bulblet is protected with one fine translucent layer of film with 2–5 layers of peels called inner peels. All tunicated cloves are surrounded by one common tunic. The inner peel is composed of cellulose, hemicellulose, lignin, and pectin (Caglar and Aydinli, 2018) leaves, and peels of them have taken considerable attention for various purposes. The biomass and wastes in recycling of matter and recuperation of chemicals with thermochemical conversion techniques are an efficient way in environmental perspective. The alliaceous plant reaches huge amount and its peels take attention in terms of difficulty of recycling with potential valuable compounds like its pulp. Here the pyrolysis of this garlic peel wastes was accomplished to obtain various valuable solid and liquid products that were analyzed with miscellaneous methods (thermogravimetric analysis/differential thermal analysis, gas chromatography/mass spectrometry, and scanning electron microscope). The bulblets commonly known as garlic cloves have been consumed for health-enhancing properties, such as cardio-protective, immune-enhancing, antioxidant, antimicrobial, anti-cancer, anticarcinogenic properties, and many others (Hussein et al., 2017; Prasad et al., 2002). These properties could be attributed to the presence of bioactive and organosulphur compounds. S-allyl-L-cysteine sulfoxide (present in cytoplasmic cells) is one of the predominant compounds that react in the presence of allinase (present in vacuole cells) to form diallylthiosulfinates (allicin), an active unstable compound, upon disruption of cells on cutting or crushing (Block, 1992; Singh et al., 2017). Pyruvic acid and ammonia are also produced during this reaction. The resulting pyruvic acid is thus correlated with the extent of garlic pungency. Apart from several bioactive compounds, it also contains a meagre amount of anti-nutritional compounds, namely, tannins, saponins, phytic acid, flavonoids, and steroids (Yusuf et al., 2018).

The literature has reported that manual peeling (MP), normal water peeling (NWP), hot water peeling (HWP), flame peeling (FP), and lye peeling (LP) and mechanical or abrasive peeling are the peeling methods used in fruits and vegetables. Manual peeling of garlic is carried out with the help of a knife or manually without the use of any specialized devices. MP is found to be labour intensive and has limitations regarding being adopted on an industrial scale, considering the economics of the process. In NWP and HWP, the outer peel of the garlic absorbs the water and becomes slightly soft, thus makes peeling easier. However, in the case of FP, the peel is burnt on a flame, which often leads to the development of a burnt flavour. Mechanical peeling is carried out using the application of an abrasive material, but it also causes the damage to the flesh portion, which may affect the quality of the garlic, particularly its organosulphur and bioactive compounds. Therefore, this method was not selected in our research plan. Lye peeling is carried out by exposing the materials to sodium hydroxide solution (Li, 2020). The aqueous alkali pre-treatment affects lignin and hemicellulose by altering the glycosidic and ester chains. It also enhances the swelling process of cellulose bundles. Hence, this results in the loosening or the breakage of lignin structures depending on the concentration of alkali used (Pawongrat, 2015).

Garlic has been utilized in various different forms since antiquity, especially in India. Besides its utilization in the form of paste, powder, flakes, and pickle, it is used in the preparation of products such as ketchup, stews, mayonnaise, curry powders etc. Garlic is also used for various therapeutic and medicinal purposes, which has significantly increased the demand for peeled garlic. Garlic peeling is the most crucial step in its processing, and also a rich source of various phytochemicals. Thus, it becomes important to know the effect of the different peeling methods on the chemical properties, organosulphur compounds, and antioxidant, anti-nutritional, and morphological properties of the garlic.

MATERIALS AND METHODS

Materials

Garlic bulbs of Haryana garlic-17 (HG-17) variety were procured from Choudhary Charan Singh Haryana Agricultural University, Hisar (29.14°N, 75.72°E),

Haryana, India, where they were sown, by adapting the standard cultivating and harvesting practices. Briefly, garlic in the form of cloves was sown in the last week of October. Pre-irrigation was done for better sprouting of cloves in the field. During the cultivation period, irrigation was carried out at an interval of 10–12 days for the first 90 days when the atmospheric temperature was low (below 20°C) and was irrigated at an interval of 7 days when the atmospheric temperature tended to increase above 20°C. Fertilizer (a mixture of 1.5% urea and 0.5% zinc sulphate) was given three times (during the cultivation period) at an interval of 15 days as per the prescribed manner. It was harvested approximately 170 days after sowing after the garlic leaves had been dried. Garlic cloves were separated from the whole bulbs. Similar-sized garlic cloves were sorted and used in the current study.

L-cysteine and L-ascorbic acid were purchased from Loba Chemie Pvt. Ltd., Mumbai, Maharashtra, India. 5,5'-dithio-bis-(2-nitrobenzoic acid) (DTNB) reagent was purchased from Himedia Laboratories Pvt. Ltd., Mumbai, Maharashtra India. (4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPS) buffer was purchased from Central Drug House Pvt. Ltd. Dahej, Gujarat, India. 2,4 dinitrophenylhydrazine (DNPH) and sodium pyruvate were purchased from Nice Chemicals Pvt. Ltd., Kochi, Kerala India. Other chemicals utilised in the current research work were of analytical grade.

Garlic sample preparation

Garlic cloves were peeled with manual peeling (MP), normal water peeling (NWP), hot water peeling (HWP), flame peeling (FP), and lye peeling (LP) methods. In the normal water and hot water peeling methods, the garlic cloves were immersed in distilled water (1:5, w/v) at room temperature and in hot water at 80 ±5°C for 7 min, respectively. The outer peel was removed for the flame peeling by placing the cloves on burning LPG gas. The garlic cloves (1:5, w/v) were immersed in freshly prepared lye solution (12% NaOH, w/v) in the LP method. The lye solution temperature was maintained at 40 ±2°C, and a 7 min immersion time was given in an agitated condition. The lye-treated garlic cloves were rubbed gently under running tap water to remove the peel and alkali from the surface. Then, cloves were immersed in the mild citric acidic solution to neutralize residual alkali.

Surface moisture was removed using tissue paper and kept under the fan at room temperature. The treatment was carried out in triplicates. To obtain garlic juice, the peeled garlic cloves were crushed in a mortar and pestle without adding water, and the crushed mass was filtered using nylon cloth. The garlic juice extracted using different peeling methods was kept in the glass vials and used without delay for analytical purposes.

Estimation of chemical properties

The pH of garlic juice was estimated using a calibrated digital pH-meter (model: LMPH-10, make: Labman scientific instruments Pvt. Ltd., Chennai, Tamil Nadu, India). Total acidity was estimated following the standard method (AOAC, 2006), and the results were expressed in terms of percentages of citric acid on a fresh weight basis. Garlic juice's total soluble solids (TSS) were measured using digital refractometer (model: HI96801, Hanna Equipments Pvt. Ltd., Raigad, Maharashtra, India). The amount of reducing sugar present in the peeled garlic cloves was measured using the described method (Miller, 1959). The garlic extract was prepared using 2.0 g (approx.) of garlic and 25 ml of distilled water, and it was filtered. 1.5 ml of filtered extract was put in the test tube and 1.0 ml of dinitro-salicylic (DNS) reagent was added. The test tube solutions were mixed thoroughly and heated in the water bath (model: MTPH049, make: Micro technologies, Ambala, Haryana, India) for 5 min. Next, 7.5 ml distilled water was added and cooled down immediately using an ice bath. Absorbance was observed at 540nm wavelength using UV-Vis spectrophotometer (model: DR6000, make: HACH company, USA). The reducing sugar was expressed in terms of mg/g, fresh weight, considering glucose as a standard solution. The titration method was used to measure the amount of ascorbic acid present in the garlic samples (Ranganna, 1997). Approximately 1.0 g of garlic was taken for the preparation of garlic extract using 25 ml of 4% oxalic acid (w/v). It was then centrifuged (model: PR-24, make: Remi, Mumbai, Maharashtra, India) at 8000 rpm for 30 min to obtain a clear extract. Then, 10 ml of garlic extract aliquot and 10 ml of 4% oxalic acid were placed in a 250 ml conical flask and titrated against 2,6-dichlorophenol indophenol reagent (TVs) up to the appearance of a faint pink color, which persisted for a few minutes. Next, 5 ml of 0.1 mg/ml

standard L-ascorbic acid solution and 10 ml of 4% oxalic acid were taken in a 250 ml volumetric flask and titrated against 2,6-dichlorophenol indophenol reagent. The ascorbic acid concentration was estimated by the following equation 1:

$$\text{Ascorbic acid} \left(\frac{\text{mg}}{\text{g}} \right) = \frac{C_{std.}}{TV_{std.}} \times \frac{TV_s}{V} \times \frac{TV}{W} \quad (1)$$

where $C_{std.}$ is the concentration of standard solution taken for titration, $TV_{std.}$ is titre volume used for standard solution, TV_s is titre volume used for sample, V is sample volume taken for titration, TV is total sample volume made, and W is the weight of sample.

Estimation of allicin content

The spectrophotometric method was used to estimate the allicin content in the garlic samples (Feng et al., 2019). 1.0 g (approx.) of garlic sample was crushed with 10 ml of 50 mM HEPS buffer which had a pH of 7.5. The crushed mixture was kept for 15 min at room temperature, and then it was centrifuged at 9000 rpm for 15 min. The supernatant was carefully separated and used to estimate the allicin content. Then, 1.0 ml of garlic extract was mixed with 5.0 ml of 10 mM L-cysteine solution in the test tube (capacity: 25 ml) and kept for 15 min. Next, the mixed reagent of 0.2 ml was diluted to 20 ml using 50 mM HEPS buffer. The diluted reagent was mixed with 0.5 ml of 1.5 mM DTNB reagent in 4.5 ml and kept for 15 min. In a control sample, the HEPS buffer was used in place of garlic extract. The absorbance of the garlic sample (A_{GS}) and control sample (A_{CS}) was measured at a 412 nm wavelength using a UV-Vis spectrophotometer. The concentration of allicin in the garlic sample was calculated using equation 2.

$$C_{\text{Allicin}} \text{ mg/100 g} = \frac{(A_{GS} - A_{CS}) \times D \times V \times 0.004}{W} \times 100 \quad (2)$$

where D is the dilution factor, V is the extraction volume, and W is the weight of the sample.

Estimation of pyruvic acid content

Pyruvic acid is a stable compound obtained by the action of allinase enzyme on S-alk(en)yl-L-cysteine sulfoxides (ACSOs) when garlic cloves are crushed. It was estimated using the method (Lucena et al., 2016) with minor modifications. 10.0 g of peeled

garlic cloves was crushed with the help of a pestle and mortar (material: ceramic, make: Labco, Ambala, Haryana, India). The extracted juice was filtered with the help of a 0.45 μm nylon syringe filter (material: Nylon-66 membrane filter, make: Riviera glass Pvt. Ltd., Mumbai, Maharashtra, India). 0.2 ml of garlic juice was mixed with 1.5 ml of trichloroacetic acid (5%, w/v) and 18.3 ml of distilled water with the help of a vertex mixer. Then, 1.0 ml of the mixed solution, 1.0 ml of DNPH having a strength of 0.0125% (w/v), and 1.0 ml of distilled water were taken into the test tube and mixed thoroughly. It was then heated to 37°C for 10 minutes and cooled down. In a similar test tube (capacity: 25 ml), 5.0 ml of NaOH solution was added having a concentration of 0.6 N and kept for 5 min to develop a yellow color. The absorbance of the sample was measured at a wavelength of 420 nm using UV-Vis spectrophotometer. The presence of pyruvic acid in all the garlic samples was calculated in terms of $\mu\text{mol/ml}$ of pyruvic acid, considering sodium pyruvate as the standard. The standard curve was prepared using six concentrations (0.0, 0.2, 0.4, 0.6, 0.8, and 1.0 millimole/ml) of sodium pyruvate (Fig. 1). The concentration of pyruvic acid in the garlic sample was estimated using Figure 1 and equation 3.

$$C_{\text{Sample}} = C_{SC} \times \frac{V_t}{V} \quad (3)$$

where C_{Sample} is the concentration of pyruvic acid in the garlic juice, millimol/ml of pyruvic acid, C_{SC} is the

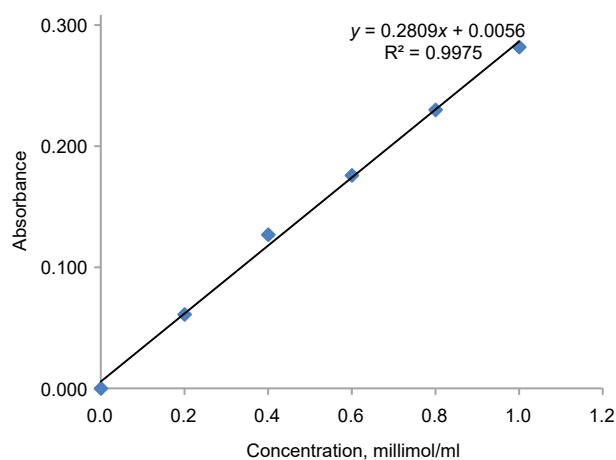


Fig. 1. Standard curve of sodium pyruvate

concentration of pyruvic acid estimated from standard curve, millimol/ml of pyruvic acid, V_t is the total volume made for estimation, ml, V is the garlic juice taken for estimation, ml.

Extraction of garlic extracts and estimation of total phenol content (TPC), total flavonoid content (TFC), and antioxidant activity (AOA)

A solvent extraction technique was used for the extraction of garlic extract. For this technique, 1.0 g peeled garlic was crushed using 5 ml of 90% methanol (v/v) containing 0.01N HCl solution, and the final volume was made up to 25 ml. The mixture solution was kept for 7–8 h at room temperature and centrifuged at 9000 rpm for 15 min. The supernatant obtained was decanted and stored in a glass vial for further use at a refrigerated temperature.

The TPC in the garlic extract was estimated using Folin-Ciocalteu reagent method with a slight modification (Lu et al., 2011). In brief, 5 ml of diluted Folin-Ciocalteu reagent was added to 1 ml of garlic extract. Next, 4 ml of Na_2CO_3 (7.5% w/v) solution was added and incubated in the dark chamber for 90 min. The absorbance was measured at a wavelength of 765 nm using a UV-Vis spectrophotometer against the blank sample. Gallic acid was taken as a standard solution for the preparation of the TPC curve. The standard curve was prepared by using different concentrations of gallic acid (0.01, 0.02, 0.03, 0.04, 0.05, 0.06, 0.07,

0.08 and 0.09 mg/ml) in place of the garlic extract sample (Fig. 2). The concentration of gallic acid was estimated from Figure 2 and TPC was calculated in terms of mg of gallic acid per gram of fresh garlic using equation 4.

$$TPC = \frac{\text{Concentration of gallic acid} \times \text{Volume of garlic extract taken}}{\text{Weight of garlic}} \quad (4)$$

The TFC of the garlic extract was estimated using the spectrophotometric method (Bhandari and Rajbhandari, 2015). In brief, 1.0 ml of garlic extract was added to 4.0 ml of distilled water. In the same test tube, 0.3 ml NaNO_2 (5%, w/v), 0.3 ml AlCl_3 (10%, w/v), and 2 ml NaOH (1 M) were added at the initial stage, 5 min, and 6 min intervals, respectively. The final volume was made up to 10 ml by adding distilled water. The absorbance was measured at a wavelength of 510 nm against the blank sample. A standard calibration curve was plotted using quercetin as a standard. The standard curve was prepared by using different concentrations of quercetin (0.01, 0.02, 0.03, 0.04, 0.05, and 0.06 mg/ml) in place of a garlic extract sample (Fig. 3). The concentration of quercetin was estimated from Figure 3 and TFC was calculated in terms of mg quercetin per gram of fresh garlic using equation 5.

$$TFC = \frac{\text{Concentration of quercetin} \times \text{Volume of garlic extract taken}}{\text{Weight of garlic}} \quad (5)$$

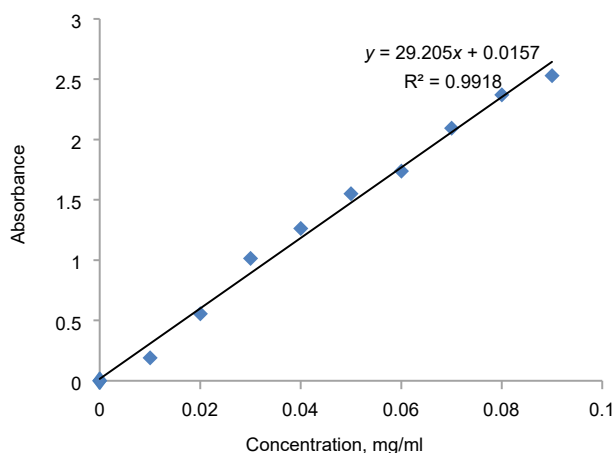


Fig. 2. Standard curve of gallic acid

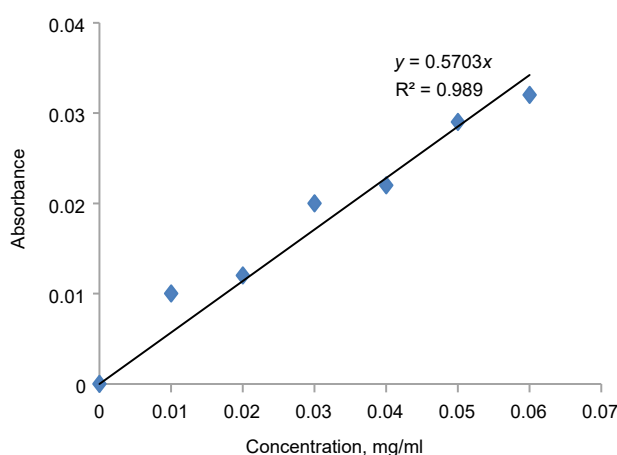


Fig. 3. Standard curve of quercetin

The AOA of the garlic extract was estimated by the 2,2-diphenyl-1-picrylhydrazyl (DPPH) method (Kinalski and Noreña, 2014) with minor modifications. In brief, 0.3 ml of garlic extract was added to 11.7 ml of 0.1 mM DPPH reagent (*w/v*). The absorbance of the sample was measured at a 515 nm wavelength using acidic methanol as a blank. The control sample was prepared with 0.3 ml of distilled water and 11.7 ml of 0.1 mM DPPH reagent. It was calculated as a percentage using equation 6.

$$AOA = \left[1 - \frac{\text{Absorbance of the sample}}{\text{Absorbance of the control}} \right] \times 100 \quad (6)$$

Estimation of anti-nutritional properties

Tannin. The spectrophotometric method was used to estimate the tannin content in the garlic sample (Onyeneke, 2018). In brief, 2.0 g (approx.) of peeled garlic clove was crushed using 20 ml of distilled water. The crushed garlic was mixed thoroughly in the test tube using an automatic shaker for 30 min. It was then centrifuged, and the supernatant was decanted. 5 ml of supernatant, 2 ml of Folin-Denis reagent, and 5 ml of saturated Na_2CO_3 were mixed in a 100 ml volumetric flask. At the same time, the tannic acid standard solution was prepared using 5 ml of a known concentration of tannic acid in place of 5 ml of supernatant. The total volume was made to 100 ml using distilled water and kept at room temperature for 90 min for incubation. The blank sample was prepared using distilled water, Folin-Denis reagent, and Na_2CO_3 solution. The absorbance was measured at 760 nm against the blank sample and expressed in percentage of tannin on a fresh weight basis using equation 7.

$$\text{Tannin (\%)} = \frac{A_{ts} \times V_{ea} \times C \times 100}{A_{ss} \times V_e \times W} \quad (7)$$

where A_{ts} is the absorbance of test sample, A_{ss} is the absorbance of standard solution, C is the concentration of standard solution, W of the weight of sample, V_e is the total volume of extract made, and V_{ea} is the volume of extract taken for analysis.

Saponin. The saponin content in the garlic samples was estimated by the method (Obadoni and Ochuko, 2002) with a slight modification. In brief, 2.0 g of garlic paste was mixed with 44 ml of freshly prepared 20% aqueous ethanol (*v/v*). It was heated at 55°C in a water bath

with continuous agitation for 4 h. The mixed solution was filtered and mixed with 44 ml of 20% aqueous ethanol. The solution was heated at 90°C in a water bath until the volume reached nearly 40 ml. The remaining extract was transferred into a 100 ml separating funnel, and then 8 ml of diethyl ether was added and thoroughly mixed. It was kept for 2 h to separate the aqueous layer from the ether layer. This practice was followed twice for the purification of saponin. Next, 6 ml of n-butanol was added to an aqueous layer, and the pooled solution was washed twice using 2 ml of 5% sodium chloride solution (*w/v*). The solution was heated in a water bath and in a hot air oven. It was expressed as a percentage of saponin on a fresh weight basis.

Phytic acid (PH.A). The amount of phytic acid in the peeled garlic sample was estimated using titration (Ovuakporie-Uvo et al., 2019). In brief, garlic extract was prepared using 0.2 g of garlic sample and 100 ml of a 2% hydrochloric acid solution (*v/v*). Then, 50 ml of the filtered solution was added along with 10 ml of distilled water and 10 ml of a 0.3% ammonium thiocyanate solution (*w/v*). It was titrated against ferric chloride solution (0.00196 g Fe/ml). The endpoint was identified by the appearance of a yellow color for a few minutes. Its concentration was expressed as a percentage of phytic acid on a fresh weight basis using equation 8.

$$\text{Phyticacid (\%)} = \frac{\text{Titre value} \times 0.00195 \times 1.19}{2} \times 100 \quad (8)$$

Field emission-Scanning Electron Microscopic (FE-SEM) and Energy Dispersive X-ray Spectroscopy (EDS) analysis

FE-SEM (JSM-7610, F PLUS, JOEL, Japan) attached with EDS was used to analyze the changes in morphology and element compositions of garlic peel and garlic powder samples peeled using the LP and MP methods and bits dehydrated at 45°C (Kaur and Prasad, 2022). The double-sided conductive tape was used to place the sample in powdered form; after that, the gold coating was applied over it. It was then transferred to the equipment and micrographs were captured at specific magnification.

Statistical analysis method

All the experiments were performed in triplicate. MS Excel, version 2007 was used to calculate the mean

and standard deviation values. Statistical analysis (ANOVA – Analysis of Variance) was carried out using the SPSS Software, by applying Duncan’s test at a significance level of $p \leq 0.05$. A principal component analysis under multivariate analysis was used to develop the correlation among the measured parameters and different methods of garlic peeling using Origin-Pro 2017 (OriginLab, USA) software.

RESULTS AND DISCUSSIONS

Effect of garlic peeling methods on chemical properties

Table 1 shows the effect of peeling methods (MP, NWP, HWP, FP, and LP) on the chemical parameters (pH, TSS, total acidity, ascorbic acid, and reducing sugar) of peeled garlic. A significant difference ($p \leq 0.05$) was observed in these chemical parameters of different peeling methods. The pH and TSS content were found to be significantly higher in HWP than in the other methods of peeling garlic. It was also observed that different methods of garlic peeling have no direct correlation between pH and TSS content. Total acidity and ascorbic acid content in lye-peeled garlic were significantly higher than those of the other methods adopted for garlic peeling; this may be due to the mild acid neutralizer used for alkali neutralization. Total acidity and ascorbic acid content in HWP garlic were found to be slightly lower than those of the other methods of garlic peeling. The decrease in total acidity of HWP garlic might be due to the interaction between the organic components or the action

of enzymes on the chemical components present in the garlic, particularly when induced at higher temperatures. The ascorbic acid losses might be due to the enzymes’ heat or oxidation of ascorbic acid, particularly ascorbic acid oxidase, cytochrome oxidase, and peroxidase (Nagy, 1980). The MP method of peeling garlic produced higher quantities of reducing sugar than the other. This may be because some quantity of reducing sugar was involved in the development of brown color during peel burning in FP. However, in the case of NWP, HWP, and LP, the reducing sugar in the garlic was reduced due to leaching out of the reducing sugar during the peeling process. At the same time, the reducing sugar was higher in the HWP method; this might be due to the conversion of some polysaccharides into reducing sugar at a higher temperature. Similar results were also found for the preparation of black garlic when kept at a higher temperature (Zhang et al., 2016).

Effect on alliin and pyruvic acid content

Alliin and pyruvic acid content in different methods of peeled garlic were shown in Figure 4. Alliin and pyruvic acid content showed significant differences ($p \leq 0.05$) with garlic peeling methods. The minimum amounts of alliin (131.03 mg/100 g, fresh weight) and pyruvic acid (39.81 $\mu\text{mol/ml}$ of juice) content were found in the HWP method. This may be due to the allinase enzyme in vacuole cells which denatured at a higher temperature. The maximum amounts of enzymes (peroxidase and allinase) were inactivated when garlic cloves were blanched at 80–100°C for 45–80s

Table 1. Effect of different peeling methods on the chemical parameters of peeled garlic

Peeling methods	Chemical parameters				
	pH	TSS °Brix	total acidity %	ascorbic acidity mg/g	reducing sugar mg/g
MP	6.11 \pm 0.015 ^b	38.87 \pm 0.31 ^b	0.77 \pm 0.050 ^{ab}	0.142 \pm 0.003 ^a	462.90 \pm 6.10 ^a
NWP	6.09 \pm 0.012 ^b	38.80 \pm 0.20 ^b	0.72 \pm 0.051 ^b	0.137 \pm 0.003 ^a	275.64 \pm 12.5 ^c
HWP	6.14 \pm 0.021 ^a	39.83 \pm 0.76 ^a	0.64 \pm 0.044 ^c	0.103 \pm 0.005 ^c	420.55 \pm 9.44 ^b
FP	6.10 \pm 0.015 ^b	39.33 \pm 0.29 ^{ab}	0.82 \pm 0.006 ^a	0.127 \pm 0.002 ^b	389.21 \pm 2.72 ^c
LP	6.08 \pm 0.015 ^b	39.67 \pm 0.29 ^a	0.80 \pm 0.011 ^a	0.144 \pm 0.006 ^a	335.26 \pm 2.08 ^d

Different letters within the column refers to significant difference ($p < 0.05$) of the mean value.

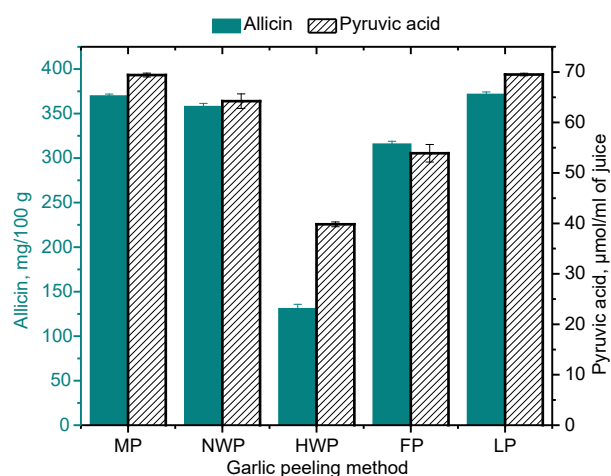


Fig. 4. Effect of different peeling methods on the allicin and pyruvic acid content of peeled garlic

(Zhang et al., 2021). Garlic peeled using the MP and LP methods showed the maximum amounts of allicin (369.84 and 371.62 mg/100 g, fresh weight) and pyruvic acid (69.40 and 69.52 µmol/ml of juice), respectively. No significant differences in allicin and pyruvic acid content were observed in these two methods. The lye solution was removed with distilled water and further neutralized with a mild acid solution, which may be the possible reason why it showed the same properties as the MP method. A significant difference in the allicin and pyruvic acid content of peeled garlic was observed in the HWP method as compared to the other method (Fig. 4). This difference may be due to the inactivation of alliinase enzyme, which may otherwise act on alliin (Block, 1992). The NWP and FP methods had a higher quantity of allicin and pyruvic acid content and were lower than the MP and LP methods.

Effect on antioxidant properties

The antioxidant properties (TPC, TFC, and percentage AOA) following different methods of peeling garlic (MP, NWP, HWP, FP, and LP) samples are mentioned in Table 2. The TPC of MP and LP garlic samples were estimated to be 260.08 and 264.69 mgGAE/100 g, which is slightly lower than the value (3.20 g of gallic acid per kg) reported for manually peeled garlic of other varieties (Toledano-Medina et al., 2016). The growing and climatic conditions, soil type, harvesting factors, and most importantly, genotypes might be responsible for this variation. A slight decrease in TPC was observed in the FP (242.54 mgGAE/100 g) and NWP (247.90 mgGAE/100 g) methods. The lower TPC (152 mgGAE/100 g) content was observed with the HWP method of garlic. Damage to heat-sensitive compounds and the involvement of phenolics in oxidation and polymerization reactions might be responsible for the reduction in TPC (Chaaban et al., 2017).

A significant ($p \leq 0.05$) difference was observed in TFC for the different methods of garlic peeling. The TFC of MP, LP, and NWP garlic samples were found to be 511.08, 517.40, and 475.01 mgQE/100g, respectively (Table 2). The results (437.92 and 444.27 mgQE/100 g) reported for the ethanolic garlic extract at 25°C for 15 and 30 min cooking times were higher for the methods adopted for MP and FP, whereas they were in line with NWP (Alide et al., 2020). A lower amount of TFC was observed in HWP (235.07 mg QE/100 g) and FP (274.33 mgQE/100 g). These variations may be due to the degradation of heat-sensitive compounds (Chaaban et al., 2017). The variation in TFC in HWP and FP may also be because at higher temperatures, the maximum number of enzymes are destroyed, resulting in the cessation of the synthesis of flavonoids.

Table 2. Effect of different peeling methods on the TPC, TFC, and AA of peeled garlic

Parameters	Peeling methods				
	MP	NWP	HWP	FP	LP
TPC, mgGAE/100 g	260.08 ±0.94 ^a	247.90 ±1.85 ^b	152.30 ±5.11 ^d	242.54 ±1.27 ^c	264.69 ±2.01 ^a
TFC, mgQE/100 g	511.08 ±2.57 ^b	475.01 ±2.53 ^c	235.07 ±2.50 ^c	274.33 ±2.45 ^d	517.40 ±1.35 ^a
AOA, %	22.53 ±0.29 ^a	20.93 ±0.23 ^b	19.04 ±0.31 ^d	19.92 ±0.46 ^c	22.82 ±0.34 ^a

Different letters within the row refer to significant difference ($p < 0.05$) of the mean value.

The results of the AOA of different methods of garlic peeling are represented in Table 2. A significant ($p \leq 0.05$) difference was observed in the different methods of garlic peeling except for MP and LP. The AOA of MP and LP garlic were found to be 22.53 and 22.82%, which is in line with the AOA result (21.69%) reported for fresh garlic (Queiroz et al., 2009). The reduction in AOA was found in garlic peeled by NWP (20.93%), FP (19.92%), and HWP (19.04%). In these methods, there was a reduction in free radical scavenging activity, which might be due to the losses of phenolic compounds and also shows a positive correlation with TPC and TFC. A similar type of observation was reported by (Queiroz et al., 2009). The reduction in AOA may be attributed to the activation of non-enzymatic reactions and intermolecular chemical reactions activated at elevated temperatures or the oozing of the chemical compounds (Chaaban et al., 2017).

Effect of garlic peeling methods on anti-nutritional properties

The effect of different methods of garlic peeling on anti-nutritional properties is represented in Figure 5. A significant ($p \leq 0.05$) amount of reduction in tannin content was observed in the peeling methods, i.e., NWP (0.00108%), LP (0.00099%), HWP (0.00094%), and FP (0.00061%) over MP (0.00115%). Similar

results have been reported for raw garlic (Udu-Ibiam et al., 2014). The reduction in tannins may be attributed to their oozing of tannins into the water and the reduction of enzymes and tannins due to heat during the processes of garlic peeling. Common beans have shown reduced tannins due to being soaked in low concentrations of sodium hydroxide solution at room temperature for 24 h (Jyothi and Sumathi, 1995).

Saponin content in manually peeled garlic was found to be 12.31%, which is slightly lower than the value (13.93 g/100 g) reported by previous results (Nwinuka et al., 2005). Lower saponin content was found in the HWP (10.95%) compared to the other methods adopted for garlic peeling, i.e., NWP (11.94%), LP (11.56%), and FP (11.23%). The reduction in saponin content might be due to losses of lipid-soluble (aglycone) and water-soluble (sugar present in their structures) compounds caused by the heat or oozing of the compounds in water during the peeling process. These compounds provide wetting, detergent, foaming, and emulsifying properties (Shanthakumari et al., 2008).

A significant ($p \leq 0.05$) amount of reduction in phytic acid content was observed in all the methods of garlic peeling over the MP (Fig. 5). Phytic acid content in the manual method of garlic was found to be 0.1088%, which is lower than the reported value

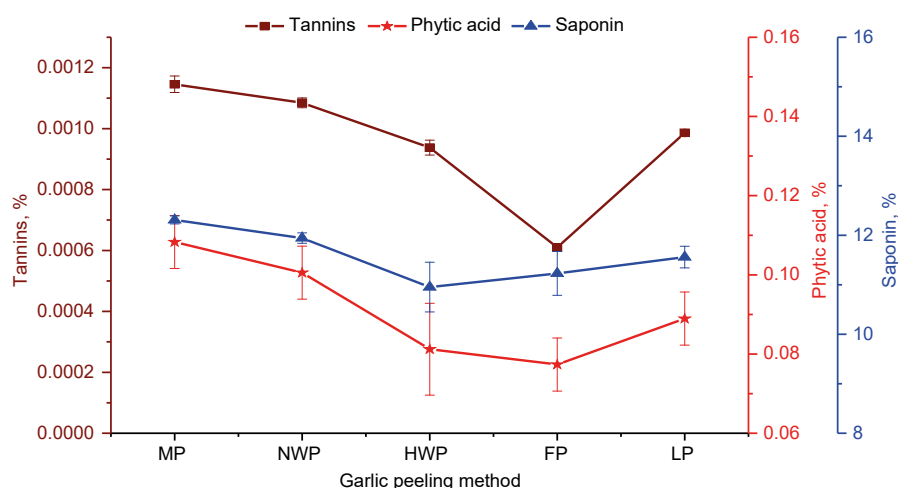


Fig. 5. Effect of different peeling methods on the anti-nutritional properties, namely, tannins, phytic acid and saponin content of peeled garlic

(0.232%) of the previous researcher (Udu-Ibiam et al., 2014). The maximum reduction of phytic acid was observed in LP (0.0735%) and FP (0.0774%). Phytic acid is known to be an anti-nutritional factor because it binds the divalent and trivalent ionic minerals, resulting in the decreased bioavailability of minerals and other nutrients. Soaking cowpea reduced the phytic acid content (Diouf et al., 2020). The phytic acid content in NWP and HWP was found to be 0.1006% and 0.0812%, respectively. The reduction of phytic acid in HWP was significantly higher due to higher temperature exposure.

Effect on morphology and EDS analysis of MP and LP

The morphology and EDS plots of garlic peel (MP and LP) and garlic powder (MP and LP; dehydrated at 45°C) samples were analyzed by a FESEM (JSM-7610, F PLUS, JOEL, Japan) analyzer attached with an energy dispersive analysis X-ray (EDX) detector (Fig. 6A–6D). There were noticeable changes in the morphological and elemental characteristics found in the garlic peel between the MP and LP methods. This could be due to the sodium hydroxide solution's ability to partially eliminate the lignin and hemicellulosic

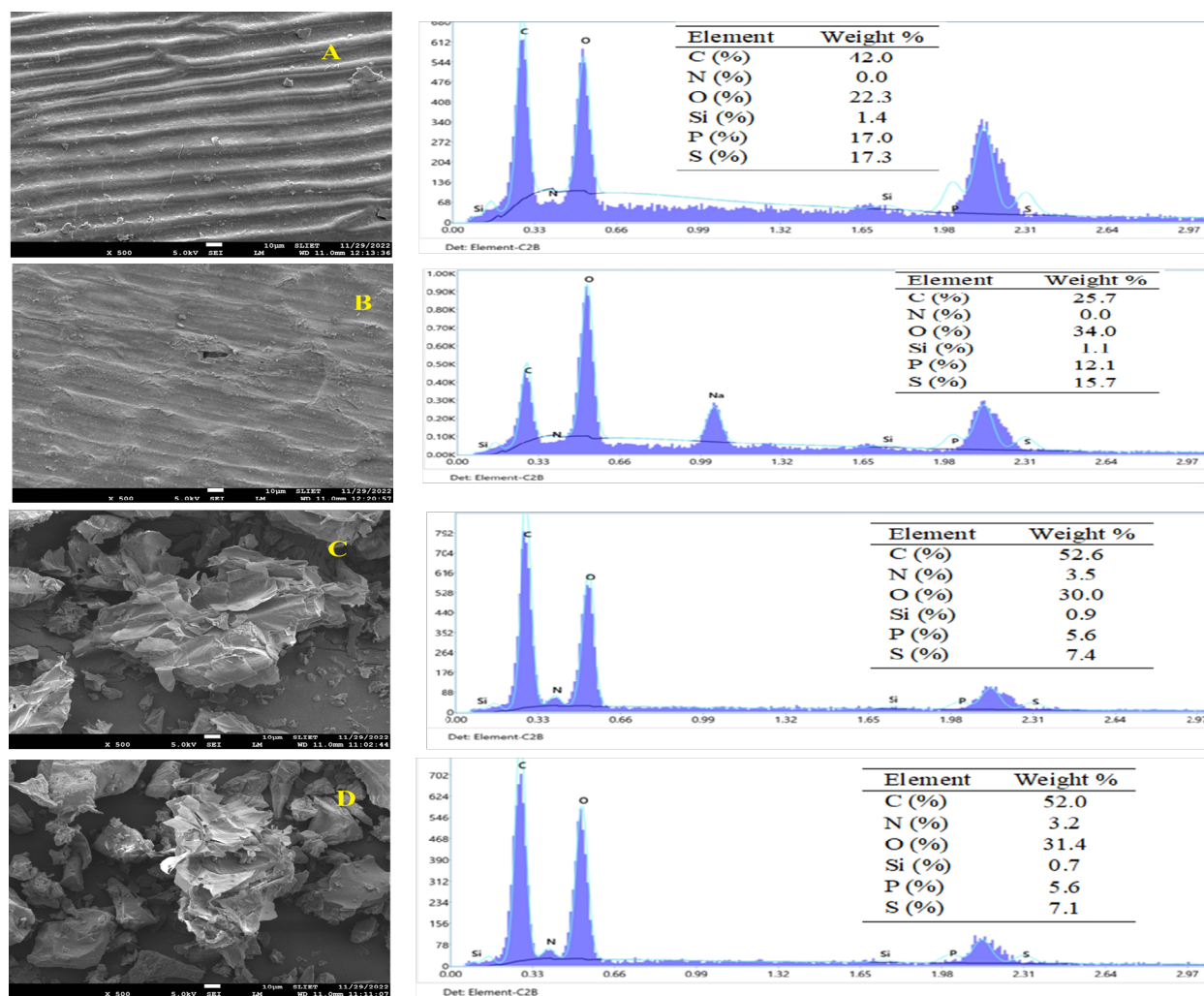


Fig. 6. FE-SEM and EDS plots of garlic peel: A – MP, B – LP and garlic powder dehydrated at 45°C: C – MP, D – LP at 500×

compounds by degrading glucosidic and ester bonds (Pawongrat, 2015). The EDS plots also showed a reduction in C, Si, P, and S elements in the lye peel over the manual peel. The garlic powder samples peeled by MP and LP showed tiny differences in morphological structure. The EDS plots also showed an equivalent result; insignificant differences were found in the identified elements.

Principal component analysis (PCA)

The correlations were developed between the peeling methods (MP, NWP, HWP, FP, and LP) and the estimated chemical parameters (pH, TSS, acidity, ascorbic acid, reducing sugar, allicin, pyruvic acid, antioxidant properties, and anti-nutritional properties) of garlic using PCA. The biplot of PCA shows 85.20% variations when selecting the first two principal components (Fig. 7). The clusters are formed near MP, NWP, and LP with the estimated parameters. The cluster made near MP garlic was found to be dominated by TFC, AOA, SAP, TAN, and PH.A, which reflects that it is dominated by anti-nutritional properties. It can also

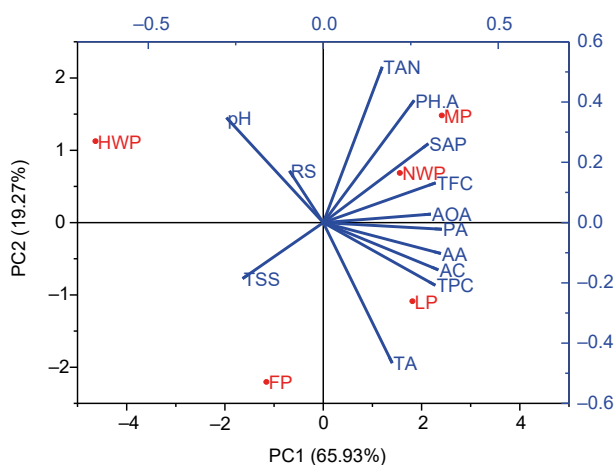


Fig. 7. Biplot of PCA of different methods (MP – manual peeling, NWP – normal water peeling, HWP – hot water peeling, FP – flame peeling, and LP – lye peeling at 12% concentration) of garlic peeling, where TSS – total soluble solid, TA – titratable acidity, AA – ascorbic acid, RS – reducing sugar, AC – allicin content, PA – pyruvic acid, TPC – total phenolic content, TFC – total flavonoid content, AOA – antioxidant activity (DPPH radical scavenging activity), TAN – tannin, SAP – saponin, PH.A – phytic acid

be observed that NWP garlic showed somewhat similar anti-nutritional properties along with beneficial chemical parameters (TFC, AOA, and PA). Hence, it may be concluded that MP and NWP are ineffective methods for producing the desired qualities in peeled garlic. The TPC showed highest positive correlation value with AC, and negative correlation with pH. Moreover, LP forms another cluster, which shows relative differences from other peeling methods of garlic. This method positively correlates with TA, TPC, AC, AA, PA, and AOA. It means positive chemical changes occurred in garlic. In this method, reducing sugar has a negative correlation. The samples dried after lye peeling were lighter in color as compared to other methods. Hence, the lye peeling (LP) method may be used to peel garlic at domestic and mass scales in food processing industries to produce various value-added products effectively without much intervention of costly labor and time-consuming process.

CONCLUSION

Multivariate analysis showed that LP had positive correlations with quality parameters among the other methods, namely, MP, NWP, HWP, and FP adopted for garlic peeling. This method slows down the sugar reducing and anti-nutritional factors with marginal differences, which helps to improve the color of dehydrated garlic and the bioavailability of nutrients as per the found reduction in the anti-nutritional properties. The LP method maintained the allicin and pyruvic acid content, which are directly correlated with the organosulfur compounds, and their presence shows better garlic quality. It also maintained antioxidant properties in comparison to manually peeled garlic. The peeling of garlic at mass scale may adopt the unit operations in the automated line by dipping the garlic cloves in the suggested solution for a specific duration, passing through light rubbing operation, neutralization, and separating the peeled garlic.

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