Research Article

Examining the polyphenol content, antioxidant activity and fatty acid composition of twenty-one different wastes of fruits, vegetables, oilseeds and beverages



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Abstract

One of the most abundantly available, cost-effective valuable resources that are of all-time concern for minimization and economical re-utilization is food waste, and quantifying the phenolic compounds and identifying the principle chemical constituents will favour their industrial exploitation potential. Water, methanol and ethanol extracts of 21 common food wastes of four different classes (fruits, vegetables, oilseeds and beverages) were screened by determination of their antioxidant activity (measured by DPPH activity, reducing power and phosphomolybdenum method) as well as total phenol, flavonoid and ascorbic acid contents. Further predominant chemical constituents (essential fatty acid composition and elemental contents) of the top four phytochemical-rich food wastes were investigated by GC–MS and ICP–MS. Water was more efficient for polyphenol extraction, and ethanol extracts for antioxidant power. Onion peel, pineapple skin and date seed had the highest phenolic content and antioxidant activity. Radish peel showed the highest ascorbic acid content (48.9 ± 1.5 mg/g). Onion peel emerged as a unique source of flavonoids (> 80%). Onion peel, radish peel and pineapple skin were identified to be the sources of essential fatty acid, i.e., linoleic acid, particularly radish peel being the rich source of alpha-linoleic acid highlighting its potential for human dietary intake or as animal feed. Moreover, the screened polyphenol and unsaturated omega fatty acid-rich food wastes constituted considerable quantities of essential macro- and micronutrients. Our study demonstrates the possibility of recovering large amounts of natural phytochemicals from food wastes as alternatives to synthetics and for industrial applications.

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Graphic abstract

Food waste Food Food Water Biolertilizer/Compost Biol

'No more ONION PEEL, PINEAPPLE SKIN and DATE SEED are a waste, but a resource of commercial value and human utility.'

Keywords Food wastes · Phenols · Flavonoids · Ascorbic acid · Essential fatty acid · Elemental composition

1 Introduction

In 2011, the Food and Agricultural Organization estimated that nearly one-third (1.3 billion tons per annum) of global food production is never consumed and ends up as waste [1]. This would be ample to feed the estimated 3 billion starving human beings among the 7 billion current world populations. It is further estimated that 14% global carbon dioxide emission emanates from this food wastes, and thus, they represent an environmental problem for management locally, regionally and internationally. Organizations are thus now pointing out the need to understand this phenomenon. The united nation estimates that by 2050 the world population is expected to reach 9 billion people and food production to increase by 70% to meet the extra demand [2]. This will increase the mass of food wastes on the earth even more, leading to potentially alarming pollution impacts. If we are able to manage food wastes efficiently, then it will be easier to combat global warming and protect life on earth. There are already initiatives to prevent food wastage. Society's present primary concern, however, is largely an economic one.

In the light of the above issues, an effort was made in the present study to identify the natural polyphenol, ascorbic acid and essential fatty acid-rich food wastes with high antioxidant potential as these bioactive compounds are considered to have a beneficial effect on health. Industries and households are the major sources of food wastes, and detailed studies of those originating from these two sources, especially from the households, are meagre. Our study thus mainly focused on domestic food wastes along with some common industrial wastes such as pomace and pulp from agricultural by-products. Since fruits, vegetables, oilseeds and beverages are the most common food classes consumed and discarded daily either fresh or dry with intact phytochemical profiles, these four classes were considered for initial evaluation.

Evaluating the phytochemical compounds in green wastes gives the potential to use the biocompounds (phenols, flavonoids, tannins, flavonols, vitamin C, vitamin E, essential fatty acid, etc.) or the antioxidant-rich sources in cosmetic, pharmaceutical and food industries as an alternative to the synthetic products. The latter are increasingly being rejected by consumers in the light of health-related issues. The most economical exploitation strategy for underutilized resources such as food wastes is to exploit them in the food production cycle by recognizing their potential. The most common re-utilization approach is the production of food supplements, oral antioxidants, dietary fibre concentrates or preservative food additives from biocompound-rich natural sources used in the foodprocessing industries. Moreover, radical scavengers and flavonoid-rich natural sources can be used as beneficial phyto-protection and anti-ageing ingredients in cosmetic products [3]. Another significance in assessing the biophenols is their value in fertilizer or compost production [4]. They are nutritionally rich with phytotoxicity and antimicrobial properties that can help to support environmental balance and sustainable agricultural production. Further, as dietary antioxidants afford protection against oxidative damage and are presumed to prevent various human diseases [5], there is also a wider prospect to produce medicines from these natural antioxidant-rich sources. Even nanoparticles can be synthesized from polyphenol-rich natural sources which can be directly used to remediate toxins in soil and aquatic ecosystems [6]. As green synthesis of nanoparticles is an emerging field in the environmental remediation sector, currently exploring the opportunities afforded by biophenols is of much importance [7]. On the other hand, biocompound-rich sources can be used as bioadsorbents of priority for remediation of emerging pollutants of concern in the biosphere [8].

Natural polyphenols/antioxidants and polyunsaturated fatty acid are found to be promising in the prevention of human heart, cancer, psychiatric and neurological diseases [9–11]. A study by Valente et al. [12] has found that polyphenols and polyunsaturated fatty acid in diet helps boost the production of the brain stem cells (new neurons). Extracts prepared from blueberry, cranberry, blackberry, raspberry and the isolated polyphenols from strawberry including quercetin, anthocyanins, kaempferol, esters of coumaric acid and ellagic acid, were found to have anticancer potential [13, 14]. The inhibition of tumorigenesis by tea preparations and its polyphenol constituents such as epigallocatechin-gallate and theaflavin have also been reported [15]. Bioactive compound-rich natural resources have thus got potential for wide applications especially in biomedical applications [16].

From an overall economic and environmental perspective, in order to exploit underutilized wastes as valuable resources more extensively and effectively, it is timely to quantify the phenolic compounds and identify the principle chemical constituents. As domestic food wastes are the most abundant, feasible, cheap resources that could be explored and managed, our study evaluated and compared the useful properties of the phenolic fractions and antioxidant power of the most common food waste classes. Fatty acid and elemental composition of the screened phenolic antioxidant-rich food wastes were also elucidated in order to get a brief overview of a resourceful food waste that can be harnessed for commercial purposes.

2 Materials and methods

2.1 Samples

The samples investigated were the residues of 21 food samples (fruits, vegetables, oilseeds and beverages) procured from local markets in South Australia. Powders of peel, skin, seed and spent coffee grounds were prepared from 14 of them. Pulp- and pomace-based powders were formulated from the remaining 7. Orange (Citrus sinensis), watermelon (Citrullus lanatus), honeydew (Cucumis melo), banana (Musa paradisica), butternut (Cucurbita moschata), pineapple (Ananas comosus), potato (Solanum tuberosum), onion (Allium cepa), radish (Raphanus sativus), garlic (Allium sativum) and peanut (Arachis hypogaea) were cleaned, manually peeled and the peels/rinds/skin/shell cut into small pieces and dried in a temperature-controlled room (37 °C) for two weeks. Subsequently, apple (Malus domestica), strawberry (Fragaria ananassa), plum (Prunus domestica), grape (Vitis vinifera), tamarind (Tamarindus indica), carrot (Daucus carota) and olive (Olea europaea) were grated, homogenized and filtered for separating the juice. The pomace or pulp left after juice extraction was dried in a forced air oven at 40 °C for 72 h. Similarly, date (Phoenix dactylifera) seed, spent coffee grounds (Coffea arabica) and tea (Camellia sinensis) leaves were also dried. After complete drying, the samples were finely ground with a coffee grinder to a particle size of approximately 0.5 mm and were stocked for further study in sealable polythene bags in a desiccator.

2.2 Extraction procedures for polyphenol compounds and ascorbic acid

Five mL of boiled water was added to 0.1 g of the sample, and the suspensions were left for 24 h in a shaker at room temperature (24 ± 2 °C). The extracts were then centrifuged for 10 min at 3000 rpm and the supernatant collected at 4 °C and used within 24 h. Similarly, supernatants were saved by replacing boiled MQ water with methanol, ethanol and trichloroacetic acid. Extracts of water, ethanol and methanol were used to determine phenols, flavonoids and antioxidant activities of the selected food wastes. Ascorbic acid content of the selected samples was determined using the trichloroacetic acid extracts. All samples were extracted in duplicate. In all the experiments, the respective standard solution was used as the positive control. Methanol or water (instead of sample extract) was used as negative control.

2.3 Determination of phenolic compounds

2.3.1 Total polyphenols (TP)

Total polyphenol content was determined in all the water, methanol and ethanol extracts following a modified version of the Folin–Ciocalteu's method [17]. About 250 µL of Folin-Ciocalteu phenol reagent was added to 100 µL extract, and the mixture was kept at room temperature (24±2 °C) for 5 min. One mL of 20% sodium carbonate was added to the mixture and vortexed gently. The total volume of the mixture was then adjusted to 5 mL with MQ water. After the mixture had been kept at 24±2 °C for 45 min, absorbance of the developed blue coloured complex was read spectrophotometrically at 660 nm against a blank, using a Synergy™ HT (Bio-Tek^R Instruments, Inc., Vermont, USA) Multi-Detection Microplate Reader. The standard calibration curve was plotted using gallic acid (25-1000 ppm) and the total polyphenol content expressed as gallic acid equivalents. Each result value was calculated as a mean of three determinations.

2.3.2 Total flavonoids (TFd)

Flavonoid content was measured by a modified spectrophotometric assay [18]. The reaction mixture comprised 100 μ L of extract, 100 μ L of 10% aluminium chloride and 100 μ L of 1 M potassium acetate solutions. After 30 min incubation at room temperature, absorbance of the yellow coloured mixture was measured at 415 nm using a microplate reader. The total flavonoid contents were then calculated and expressed as quercetin equivalents.

2.4 Screening of the extracts for antioxidant potential

Natural polyphenols derived from plant materials are well known for their antioxidant potential [19], which does not result from a single mechanism but includes a wide range of reactions. As no one method can evaluate them all, it is typically recommended to use more than one technique to evaluate the antioxidant potential of samples. Thus, three different methods were employed as detailed below.

2.4.1 DPPH radical scavenging activity (DPPH Inhibition)

DPPH radical scavenging activity of the food waste extracts was evaluated according to a method outlined by Blois [20] with slight modifications. Briefly, 60μ M of DPPH (2,2-diphenyl-1-picrylhydrazyl) radical solution in methanol was prepared and 3.9 mL of this solution mixed with 100 µL of the sample solutions (containing their respective phenol fractions). After 30 min, absorbance of the samples (As) was measured at 515 nm. Blank samples containing 100 µL of the respective extractant was simultaneously treated as above and its absorbance recorded as A_b. DPPH radical scavenging activity was then calculated using the formula given below:

%DPPH inhibition =
$$\frac{A_{b-A_s}}{A_b} \times 100$$

2.4.2 Reducing power (P_R)

Reducing power of phenolics present in the extracts was estimated using a method as described by Oyaizu [21]. About 100 μ L of extract, 500 μ L of phosphate buffer (0.2 M, pH 6.6) and 500 μ L of potassium ferricyanide (1%) were vortexed gently and incubated at 37 °C in a water bath. After 20 min, 500 μ L of trichloroacetic acid (10%) was added to the mixture and the contents were centrifuged at 5000 rpm for 10 min. The upper layer (500 μ L) was then collected separately and mixed with 100 μ L of iron (III) chloride solution (0.1%), and the absorbance measured at 700 nm. Ascorbic acid was used as the standard. Increased absorbance of the reaction mixture signifies greater ferric to ferrous ion-reducing power of the food wastes tested.

2.4.3 Total antioxidant activity by the phospho-molybdate method ($P_{\rm M}$)

The antioxidant activity was evaluated by the phosphomolybdate method of Prieto et al. [22], with slight modifications. The basic principle is the reduction of Mo(VI) to Mo(V) by the sample extract possessing antioxidant compounds. Briefly, an aliquot of 100 μ L of the sample solution was combined with 1 mL of the reagent solution (0.6 M sulphuric acid, 28 mM sodium phosphate monobasic and 4 mM ammonium molybdate) in Eppendorf tubes. For the blank, the respective extractant (100 μ L) was mixed with 1 mL of the reagent and the tubes were capped and incubated in a water bath at 95 °C for 90 min. After 90 min, samples were cooled to room temperature and the absorbance measured at 695 nm against ascorbic acid.

2.5 Ascorbic acid (AA) content

Vitamin C concentrations in the food waste trichloroacetic acid extracts were determined using the method of Roe and Kuether [23]. The supernatant (500 μ L) was mixed with 10 μ L of DTC reagent (3% of 2, 4-dinitrophenylhydrazine, 0.4% of thiourea and 0.05% of copper (II) sulphate) prepared in 9 N sulphuric acid, vortexed gently and incubated at 37 °C in a water bath for 90 min. After incubation, the mixture was ice-cooled followed by the addition of 750 μ L of 65% (v/v) sulphuric acid, and the absorbance of the mixture measured at 520 nm. The results were expressed as ascorbic acid equivalents.

2.6 GC and ICP-MS analysis

Predominant chemical constituents of the top four phytochemical-rich food wastes were investigated by GC-MS. Briefly, hot water extract of the food wastes was acidified with few drops of concentrated HCl, extracted by ultrasonication for 15 min (12 kHz sweep bandwith, Soniclean Pulse Swept[@] Power Ultrasonicator, Soniclean Pty. Ltd., Australia) with methanol, filtered (0.4 μ filter) and injected in a GC 5975 VL mass selection detector equipped with triple axis detector (Agilent Technologies, USA). The GC injection port was configured for 1 µL on-column injections, with an initial temperature of 50 °C, held for 5 min, and ramped up to 260 °C in 20 min. The flow rate was 1.1 mL min⁻¹ with a total run of 77.5 min. An Agilent HP-5MS capillary column with 5% (v/w) phenyl-substituted methyl siloxane nonpolar stationary phase, cross-linked and double bonded to the capillary wall with excellent thermal stability and low bleed levels was used. The dimension of the column was $30 \text{ m} \times 250 \text{ } \mu\text{m} \times 0.25 \text{ } \mu\text{m}$. From the obtained chromatogram, the unknown compounds were identified by matching their specific retention time with the existing database. Compounds that presented more than 80% similarity with the existing database are only presented. Since majority of the food waste constituents were fatty acid, we observed fatty acid methyl esters as briefed in Table 3.

The phenol and essential fatty acid-rich food wastes were analysed for total carbon (C) and nitrogen (N) by dry combustion with a Trumac CN analyzer (Leco[®] Corporation, US). Subsequently, portion (0.5 g) of the food wastes were digested in triplicate with 5 mL *aqua regia* in a Teflon digestion vessel using a microwave accelerated reaction system (CEM-MARS X[®]) as outlined in US EPA method SW 3051. The total elemental (mineral) contents in diluted suspensions of the extracts were determined using a standard reference material (Montana soil SRM 271, Certificated by National Institute of Standards and Technology) and blank in an Agilent 7500c (Agilent Technologies, Japan) inductively coupled plasma mass spectrometer (ICP–MS).

2.7 Statistical analysis

All experimental results were reported as mean values with their corresponding standard deviations. Differences between variables were tested for significance by multivariate analysis and Tukey's test using SPSS (Statistical Program for Social Sciences, IBM® Corporation, USA) statistical software version 20. Differences at p < 0.05 were considered to be significant. Pearson correlation coefficients (r) were also calculated to assess the significance of correlations among variables again using SPSS software.

3 Results and discussion

3.1 TP

Polyphenols are the most significant fruit constituents by virtue of their antioxidant activity [24]. Table 1 summarizes the TP content in the water, methanol and ethanol extracts of the food residues. For all the extracts tested, the amount of TP in the fruit, vegetable, oilseed and beverage waste extracts ranged from 7-68, 9-105, 9-62 and 13-30 mg gallic acid/g dry sample, respectively. There are significant effects of different extractants on the TP content (p < 0.05); the highest was determined in the water extract for most samples analysed and was 1.1, 3.9 × higher than the TP values for the methanol and ethanol extracts. Polyphenol extraction by solvents like methanol and ethanol was observed to be best suited for peanut shell as well as spent tea leaves (1.8-2×higher), and date seed and onion peel $(1.5-3 \times higher)$. The variability in TP content caused by different solvents may be due to the varying solubility of the phenolic compounds, which is directly related to the compatibility of the compounds with the solvent system. Even the nature of the sample (solidity, pH, etc.) and extraction temperature can be factors that affect the solubility of the phenolic compounds. Overall, based upon the present TP data, it is assumed that the food wastes contain diverse phenolic compounds with different polarity, and water is a better extractant for polyphenols than the other polar protic solvents like methanol and ethanol. A study conducted by Peschel et al. [3] has demonstrated the possibility of recovering large amounts of phenolics with antioxidant properties from fruit and vegetable residues using water. However, in most cases, methanolic extraction of powders has been used to study the phytochemical profile of food wastes [25, 26].

Of the 21 food wastes considered, onion peel stands out clearly from the others in its high phenolic content (mean 75.6 mg/g), followed in rank order by date seed (47.7 mg/g) > pineapple skin (39.7 mg/g) > olive pomace \geq radish peel \geq plum pomace (30–32 mg/g) extracts.

Table 1	TP and TFd content in wa	er, methanol and ethano	l extracts of food wastes
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Food waste	TP ^a				TFd ^b			
	Water	Methanol	Ethanol	Mean	Water	Methanol	Ethanol	Mean
(a) Fruits								
Orange peel	28.8±1.6	19.1±2.8	22.0 ± 1.0	23.3	5.1 ± 0.7	6.8±1.5	8.8±1.2	6.9
Watermelon rind	15.1±2.8	13.4±2.7	8.1 ± 1.5	12.2	12.6±0.6	3.5 ± 0.7	2.9 ± 0.8	6.3
Honeydew peel	26.7 ± 0.9	24.7 ± 0.8	18.6±1.3	23.3	7.1 ± 0.7	14.6±0.6	17.2 ± 2.7	13
Banana peel	27.1 ± 0.8	24.7 ± 0.7	20.0 ± 0.2	23.9	3.1 ± 0.2	5.0 ± 0.3	8.7±1.0	5.6
Butternut peel	20.1 ± 1.2	10.7 ± 0.9	7.9 ± 2.5	12.9	11.5 ± 0.9	4.3±1.2	5.1 ± 1.3	7
Apple pomace	27.5±1.0	17.1 ± 0.4	7.6±0.6	17.4	4.1 ± 0.1	6.9 ± 0.2	3.4 ± 0.5	4.8
Strawberry pomace	37.5±1.8	21.9±1.8	13.8±2.8	24.4	1.9 ± 0.1	4.9 ± 0.07	4.1 ± 0.8	3.6
Plum pomace	51.8 ± 0.5	20.9 ± 0.6	17.6±0.1	30.1	7.4 ± 0.4	6.0 ± 0.4	5.3 ± 0.6	6.2
Grape pomace	36.8±0.7	21.3 ± 0.5	15.2 ± 2.1	24.4	5.2 ± 0.2	4.7 ± 0.3	3.4 ± 0.5	4.4
Pineapple skin	68.3±1.2	28.6±1.5	22.3 ± 0.6	39.7	15.3 ± 0.2	12.1 ± 0.8	9.8 ± 2.0	12.4
Tamarind pulp	29.0±1.1	14.2 ± 2.4	25.6 ± 0.5	22.9	7.2 ± 0.4	7.9 ± 0.6	6.6±0.7	7.2
Dates seed	37.2±1.1	38.8±1.1	67.0±5.0	47.7	3.4±2.8	2.9 ± 2.4	3.9±1.2	3.4
(b) Vegetables								
Potato peel	9.4±1.6	10.4 ± 0.2	10.7±2.3	10.2	2.3 ± 0.9	2.0 ± 0.7	4.2 ± 0.1	2.8
Onion peel	35.7±5.1	85.7±4.1	105.2±1.3	75.5	32.1±0.2	76.7 ± 0.1	74.6±1.9	61.1
Carrot pulp	34.4±2.0	15.9 ± 1.6	24.1 ± 1.4	24.8	5.3 ± 0.2	2.7 ± 0.3	8.1 ± 0.5	5.4
Radish peel	44.6±0.6	19.4±1.2	29.9 ± 1.5	31.3	5.3 ± 0.2	2.0 ± 0.6	7.1±0.2	4.8
Garlic peel	11.5±2.8	10.5 ± 1.8	4.7 ± 1.4	8.9	2.1 ± 0.7	0.7 ± 0.3	1.4 ± 0.7	1.4
(c) Oilseeds								
Olive pomace	62.2±2.8	16.0 ± 2.5	18.6±2.2	32.3	10.5 ± 0.2	3.7 ± 0.6	8.4 ± 0.3	7.5
Peanut shell	11.5±0.8	17.7±2.6	9.7±2.0	13	2.2 ± 0.4	9.0±0.3	5.8 ± 0.8	5.7
(d) Beverages								
Spent coffee grounds	29.3±0.7	26.5 ± 0.9	15.9 ± 1.5	33.9	5.7±1.9	5.0 ± 0.1	9.7±0.7	6.8
Spent tea grounds	13.5 ± 2.1	30.1±1.8	24.7 ± 1.4	22.8	2.9 ± 0.07	11.0 ± 1.0	12.2 ± 1.3	8.7

^aIn mg gallic acid/g

^bIn mg quercetin/g

Garlic, potato and butternut peels and watermelon rind recorded the lowest. Since the sample preparation, extraction and determination procedures were exactly the same in all cases, the significant differences observed among their phenolic contents in this study is probably due to the intrinsic properties of the food wastes. These substantial differences in TP values of the food waste extracts tested are likely to account for the distinct antioxidant activities among the samples. In fact, there were no significant differences between some of the food wastes like spent tea leaves and coffee grounds, tamarind pulp, orange peel, honeydew melon peel, banana peel, strawberry pomace, grape pomace and carrot pulp (mean 23.5 mg/g). Our TP values found in the food waste extracts were up to 4×higher than those previously reported in the literature. In the case of onion peel, a similar total phenol content of hot water extracts was reported by Lee et al. [27] and Singh et al. [28], although the values reported by the latter authors for onion peel methanol extracts were approximately 1.8×lower. Skerget et al. [29] observed similar values for ethanolic onion peel extracts. A wide range of TP contents was proposed for olive pomace water extracts [30] which was also in broad agreement with those reported in Table 1. However, Ardekani et al. [31] observed TP values considerably higher for date seeds than those reported in the present research (6.8–11.6 mg/g as gallic acid equivalents). The TP value determined by Kalpna et al. [32] for pineapple extract was $2 \times \text{lower than in this study.}$ Singh and Rajini [33] reported 3.93 mg gallic acid/g in potato peel extracts, 3×lower than the observation made in the present analysis. A similar report of a 3×lower TP value was made by Lu et al. [34] for garlic peel extracts. All of these differences could be attributed to the use of different extraction techniques and also to different varieties, geographic origin, growth conditions, and harvest season of samples tested as all these parameters affect the synthesis and accumulation of phenolic compounds in plant parts [35]. It is noteworthy that, apart from the samples of importance discussed above, data are not available for

radish peel, watermelon rind and butternut peel water/ methanol/ethanol extracts.

3.2 TFd

Flavonoids are one of the widely distributed groups of plant phenolic compounds which are very effective antioxidants [36]. Our results for total flavonoid content of food waste extracts after aluminium chloride and potassium acetate reaction are shown in Table 1. Significant differences were noticed between the different food wastes tested and between the different solvents used for extraction. Ethanolic extracts showed better relationship with phenols (r = 0.63, p < 0.05) than methanolic and water extracts. This might be due to more non-covalent interactions of ethanol with flavonoids [37] that would have resulted in a rapid diffusion of flavonoids in ethanol compared to methanol and water. Solubility of polyphenols depends mainly on the hydroxyl groups, molecular size and length of the hydrocarbon chains. This might also be the reason for ethanol being the best solvent for flavonoid extraction from plant materials as found by other authors [38]. Our extraction data varied between a mean minimum value of 1.4 mg quercetin/g for garlic peel and a maximum of 61.1 mg quercetin/g for onion peel, quite similar to the trend observed for the total phenolic content of the food residues. The flavonoid content of the 21 samples decreased in the following order: onion peel > honeydew peel \geq pineapple skin > spent tea leaves \geq olive pomace \geq spent coffee grounds \geq tamarind pulp \geq butternut peel ≥ orange peel > watermelon rind ≥ plum pomace > peanut shell \geq banana peel \geq carrot pulp > apple pomace \geq radish peel > grape pomace \geq strawberry pomace > date seed \geq potato peel > garlic peel. From all the food residues assessed, peels were shown to contain high amounts of flavonoids. Singh et al. [28] published the total flavonoid content of onion peel with 3.5-fold higher values for their water extracts. On the other hand, flavonoid concentration of the ethanolic extracts of onion peel is in line with the findings of Skerget et al. [29]. Kalpna et al. [32] reported a flavonoid concentration of 3.19 mg quercetin/q in pineapple skin methanolic extracts nearly $3.8 \times$ lower than the results in this study. No quantifiable amounts of flavonoids were found in the garlic peel by Beato et al. [39]. In summary, total flavonoid results found in this study were three to fourfold higher than those reported in the literature for similar food residues. We believe that this is because of the use of different analytical methods and standards. One of the significant findings of this study is that the prime source of flavonoids among all the food wastes, onion peel, accounted for > 80% flavonoids among the total phenols detected. Flavonoids were also the major constituent in butternut peel, with

a concentration of > 50% of the total phenols. In general, a weakly significant correlation was found between the total phenols and flavonoid content of the food residues (r=0.55-0.63, p < 0.05), which suggests that flavonoids are indeed one of the major phenolic compounds present in these food wastes.

3.3 Antioxidant potential

3.3.1 DPPH radical scavenging activity

DPPH is a widely used stable free radical to evaluate the antioxidant potential of a sample [40]. Comparison of the %DPPH inhibition values for water, methanol and ethanol extracts of different food waste classes are shown in Table 2. Ethanol extracts significantly (p < 0.05) showed high DPPH radical scavenging activity for most of the extracts although they contain less total phenolics in these extracts compared to the water extracts. This might be because of the differences in the phenolic combinations [41], as the DPPH radical scavenging activity of a substrate depends upon its phenolic structure as well as the number and the location of the hydroxyl groups [42]. With a mean DPPH inhibition of 70%, onion peel showed higher antioxidant capacity than that observed for garlic peel, which presented the lowest DPPH inhibition (mean: - 3.6%). Significant differences (p < 0.05) were detected among the 21 food wastes evaluated. Similar to the total phenolic contents, three of the food residue extracts exhibited the highest antioxidant activity as indicated in the following rank order: onion peel > date seed \geq pineapple skin. All the remaining extracts other than garlic peel, potato peel, butternut peel, watermelon rind, apple pomace and peanut shell (means: -6.2 to 11% DPPH inhibition) exhibited intermediate antioxidant potential (means: 30-45% DPPH inhibition). The %DPPH radical scavenging activity of onion peel found in this study is in accordance with the findings by Singh et al. [28] and Skerget et al. [29]. However, for tea waste, potato peel and strawberry pomace, the reports available in the literature [43–47] are values up to 20-fold higher than those reported here. No reports are available in the literature for rest of the samples to enable comparison.

3.3.2 Ferric and molybdenum reduction

Their reducing property signifies that antioxidant compounds are electron donors and can thus reduce the oxidized intermediates of lipid peroxidation processes [48]. It is for this reason the ferric and molybdenum reducing properties of the food wastes were evaluated to screen the best source of antioxidants (Table 2). The measured antioxidant activity varied because each assay is based

Food waste	AA content ^a	Antioxidant a	Ictivity							
		DPPH inhibiti	ion ^b		P _R c			\mathcal{P}_{M}^{d}		
		Water	Methanol	Ethanol	Water	Methanol	Ethanol	Water	Methanol	Ethanol
(a) Fruits										
Orange peel	3.7 ± 0.3	18.6 ± 0.5	27.7±0.4	52.4 ± 1.6	19.0 ± 0.7	19.2±2.1	16.5 ± 1.7	4.7±1.6	4.8 ± 0.2	5.5 ± 0.09
Watermelon rind	4.5 ± 0.2	-1.4 ± 0.1	18.1 ± 0.2	8.1 ± 0.7	4.4±0.1	12.1±2.6	7.0 ± 0.07	2.6 ± 0.07	2.7 ± 0.09	2.9±0.6
Honeydew peel	4.9 ± 0.6	5.3 ± 1.5	43.9±0.4	47.9 ± 0.6	10.2 ± 0.4	23.8±0.8	14.8 ± 0.8	2.9±0.1	7.0±0.2	4.7 ± 0.4
Banana peel	2.5 ± 0.3	9.3±0.7	44.0 ± 0.2	48.7 ± 0.9	10.2 ± 0.2	23.9 ± 0.5	16.4±1.7	3.0 ± 0.08	7.7±0.4	5.5 ± 0.04
Butternut peel	0.7 ± 0.1	4.0 ± 0.8	25.6 ± 0.8	4.9 ± 0.7	9.8±0.3	12.0 ± 1.4	5.7 ± 0.7	2.6±0.1	1.8 ± 0.2	2.9 ± 0.06
Apple pomace	4.3 ± 0.4	9.8±2.8	44.0 ± 0.6	-4.3 ± 1.4	14.2±0.2	18.7 ± 0.7	5.5 ± 1.8	3.6±0.1	4.1±0.1	2.5 ± 0.1
Strawberry pomace	7.7 ± 0.3	33.1±0.9	36.7±0.2	29.5 ± 1.8	27.4±0.1	23.3±0.6	11.1 ± 1.0	12.3 ± 0.2	6.4 ± 0.2	4.1 ± 0.2
Plum pomace	9.0 ± 1.2	36.4 ± 3.9	32.9±0.3	45.5 ± 1.0	28.9 ± 0.4	21.7±0.4	12.7 ± 0.2	14.0 ± 0.07	5.2 ± 0.6	4.5 ± 0.1
Grape pomace	7.9±0.7	28.7 ± 1.9	25.6 ± 0.4	30.2 ± 0.07	23.8 ± 0.5	23.1±0.9	11.8 ± 0.3	9.3±0.3	5.5 ± 0.08	4.2 ± 0.2
Pineapple skin	21.4±1.2	78.1±1.6	55.9±1.0	54.6 ± 0.6	35.1 ± 0.9	24.4±1.1	17.4 ± 1.3	16.0 ± 0.1	8.8 ± 0.3	5.5 ± 0.01
Tamarind pulp	14.9 ± 0.5	20.0 ± 0.3	18.9 ± 0.3	70.5 ± 1.7	20.8 ± 1.0	14.5 ± 0.9	19.3 ± 2.4	4.8 ± 0.4	3.0 ± 0.9	7.8 ± 0.04
Dates seed	4.2 ± 0.4	30.8 ± 0.4	88.4 ± 0.4	78.5 ± 0.7	24.9 ± 0.1	25.7 ± 1.5	21.2 ± 1.7	9.5 ± 0.3	10.9 ± 0.3	9.6 ± 0.07
(b) Vegetables										
Potato peel	1.6 ± 0.5	-5.7 ± 0.4	1.5 ± 0.6	17.2 ± 0.5	-13.3 ± 4.3	3.5 ± 0.7	8.8±1.6	1.9 ± 0.2	1.3 ± 0.2	3.9 ± 0.6
Onion peel	5.8 ± 0.8	28.6 ± 0.6	89.5 ± 1.0	92.1±1.3	23.7 ± 0.4	26.5 ± 2.1	21.3±1.4	9.1 ± 0.4	12.2 ± 0.4	10.9 ± 0.1
Carrot pulp	3.1 ± 0.6	23.4 ± 6.3	19.5 ± 0.3	57.0 ± 0.9	22.2 ± 2.5	16.3 ± 1.5	18.2 ± 0.4	6.2 ± 0.2	3.5 ± 0.2	5.6 ± 0.08
Radish peel	48.8 ± 1.5	33.9 ± 2.5	31.4 ± 0.3	72.8±0.6	27.8 ± 0.3	20.9 ± 0.09	19.8 ± 0.7	13.6±0.3	5.4 ± 0.3	8.5 ± 0.2
Garlic peel	1.8 ± 0.5	-4.4 ± 2.0	10.5 ± 0.2	-24.9 ± 1.9	-5.5 ± 0.7	10.3 ± 0.6	4.9 ± 0.6	2.0 ± 0.2	1.6 ± 0.2	1.8 ± 0.3
(c) Oilseeds										
Olive pomace	9.7 ± 0.2	44.7±5.6	21.9±0.1	47.0 ± 0.4	34.6 ± 0.5	16.8 ± 3.3	14.6 ± 0.9	15.8 ± 0.6	3.8 ± 0.07	4.5 ± 0.3
Peanut shell	1.3 ± 1.1	-2.9 ± 0.1	26.9 ± 0.9	11.1 ± 1.4	-0.9 ± 0.1	19.0 ± 1.3	7.3 ± 0.8	2.3 ± 0.08	4.6 ± 0.1	3.7±0.2
(d) Beverages										
Spent coffee grounds	4.9 ± 0.2	22.8 ± 0.2	47.0 ± 0.3	38.0 ± 1.0	22.1 ± 0.1	24.1 ± 0.9	11.9 ± 0.9	5.4 ± 0.2	8.1 ± 0.1	4.3 ± 0.1
Spent tea leaves	2.5 ± 0.6	-2.9±1.2	84.7±0.7	56.3 ± 1.1	-2.8 ± 0.2	24.6 ± 1.1	18.8 ± 0.6	2.2 ± 0.4	9.6 ± 0.2	7.8±1.2
^a ln mg ascorbic acid/g										

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 $^{\rm b}$ ln % inhibition at 60 μM DPPH

^cln mg ascorbic acid/g ^dIn mg ascorbic acid/g on different chemical reactions. The ferric reducing power and molybdenum reduction ranged from 0.37 to 25.9 mg ascorbic acid/g dry sample and from 1.8 to10.7 mg ascorbic acid/g dry sample, respectively. Similar to DPPH inhibition, onion peel, date seed and pineapple skin exhibited the highest and garlic peel the lowest antioxidant potential. Overall, a similar pattern as the DPPH assay was observed with slight variations. However, in the ferric and molybdenum reduction assays, antioxidant activities of the water and methanol extracts were significantly (p < 0.05) greater than for the ethanol extracts. This might be due to the presence of more hydrophilic compounds in the water extracts [49].

3.4 Ascorbic acid (vitamin C) content

As ascorbic acid is one of the endogenous antioxidants found in plant parts [50], evaluation of its level in the selected food wastes was carried out using the DTC reagent; its monitored absorbance at 520 nm is presented in Table 2. Vitamin C content of the food residues varied from 0.7 to 48.8 mg ascorbic acid/g sample on a dry weight basis, which represents a variation of about 69-fold. Radish peel showed significantly (p < 0.05) the highest ascorbic acid content (48.9 \pm 1.5 mg/g) followed by pineapple skin and tamarind pulp. Butternut peel and peanut shell had the lowest antioxidant capacity. The total ascorbic acid content of the food residues is unrelated to the total polyphenol content or antioxidant potential. This suggests that vitamin C is the minor antioxidant compound in most of the food residues tested. Further data are not available in the literature to compare the food wastes tested with the maximum or minimum ascorbic acid contents found elsewhere. In general only the vitamin C content of entire fresh fruits or vegetables is available. Compared to these, residues like peels and pulp have only 50-70% of the ascorbic acid contents. In spite of this, food wastes are clearly rich sources of vitamin C.

3.5 Correlation between assays

In order to evaluate the uniformity of the expression the activities of the food residues based on the three assays employed, Pearson's correlation coefficients were calculated. All correlations between the different methods revealed a significantly high, positive correlation ($r \ge 0.86$, p < 0.05), suggesting that they produce comparable values for their phenolic constituents and antioxidant potential. For the antioxidant assays, all the methods showed the highest correlation coefficients (r = 0.92 to 0.996, and r = 0.86 to 0.998; p < 0.05) for all the solvents tested, although strong correlation was also observed for the ethanol extracts (r > 0.995, p < 0.05). This strong correlation

between the different methods might be due to the possibility of single-electron transfer in all the three methods, in spite of their unique mechanisms. A similar correlation was previously found by Dudonne et al. [51] for plant extracts. Various authors have reported the more direct, positive correlations between the antioxidant ability results found after evaluation with different methods on a wide range of plant materials and food products [38].

It was also noted that the uniformity in the expression of the in vitro antioxidant activity of the food wastes based on the three methods is highly dependent upon the total phenol (r = 0.91 to 0.998, p < 0.05) and to some extent on the flavonoid content (r = 0.535 to 0.633, p < 0.05) irrespective of the type of solvent used for extraction. Conversely, correlation of flavonoid values with either one of the three methods was poor and not significant (p > 0.05) when the phenolic compounds are extracted using water. Additionally, no correlations were observed between the ascorbic acid content and the polyphenol profile of the food waste extracts (r = 0.13 to 0.28, at p < 0.05), in disagreement with the findings of Benammar et al. [52]. This is likely due to the use of a different reagent to extract vitamin C (trichloroacetic acid), as the type of extractant influences the extraction efficiency of bioactive compounds together with the antioxidant potential. With regard to any relationship between the antioxidant activity of onion peel extracts with the total phenol content, the correlation coefficient reported in the present study is in line with the range reported by Cioffi et al. [53] for olive pomace and Pinelo et al. [54] for grape pomace.

Regardless of the antioxidant activity assays, it is evident from Tables 1, 2 and 3 that food waste extracts with the highest total polyphenol content had higher antioxidant potential. Hence, the link between these two parameters was assessed and is presented in Fig. S1 for each of the extracts. This clearly shows the positive relationship between them irrespective of the methodologies used for all the three solvent types, with the strongest being for onion peel.

3.6 Fatty acid and elemental composition of phytochemical-rich food wastes

Results obtained by the GC–MS analysis of date seed, onion peel, pineapple skin and radish peel are presented in Fig. S2 and Table 3. In total 7, 6, 14 and 8 compounds were identified in onion peel, date seed, pineapple skin and radish peel, respectively. Fatty acids were the major portion of all the food waste samples, with essential polyunsaturated omega fatty acid–linoleic acid observed in onion peel, pineapple skin and radish peel. The majority constituent of onion peel was oxalic acid, followed by linoleic acid. Onion peel also constituted yet other

Table 3 Overview of the major constituents of polyphenol-rich food wastes methanolic extracts as examined by GC

Peak no	Rt (min)	Identified compound	Common name	Class
(a) Onior	n peel			
1	5.019	Ethanedioic acid, methyl ester (88%)	Oxalic acid	Dicarboxylic acid
2	8.618	Propanedioic acid, dimethyl ester (93%)	Malonic acid	Dicarboxylic acid
3	20.186	2-Furancarboxaldehyde, 5-(hydroxymethyl) (91%)	Hydroxymethylfurfural	Furans
4	29.862	Tridecanoic acid, methyl ester (81%)	Tridecylic acid	Saturated fatty acid
5	40.660	Hexadecanoic acid, methyl ester (99%)	Palmitic acid	Saturated fatty acid
6	44.602	9,12-Octadecadienoic acid (Z,Z)-methyl ester (99%)	Linoleic acid	Omega-6 fatty acid (essential)
7	44.714	9-Octadecenoic acid (Z)-methyl ester (99%)	Oleic acid	Monounsaturated omega-9 fatty acid
(b) Date	seed			
1	4.985	Furfural (90%)	Furan-2-carboxaldehyde	Heterocyclic aldehyde
2	20.172	2-Furancarboxaldehyde, 5-(hydroxymethyl) (83%)	Hydroxymethylfurfural	Furans
3	29.856	Dodecanoic acid, methyl ester (95%)	Lauric acid	Saturated fatty acid
4	35.520	Methyl tetradecanoate (96%)	Myristic acid	Saturated fatty acid
5	40.653	Hexadecanoic acid, methyl ester (98%)	Palmitic acid	Saturated fatty acid
6	44.602	9,12-Octadecadienoic acid, methyl ester, (E,E) (99%)	Linolelaidic acid	Omega-6 trans fatty acid
(c) Pinea	ople skin			
1	5.062	Ethanedioic acid, dimethyl ester (81%)	Oxalic acid	Dicarboxylic acid
2	11.020	Pentanoic acid, 4-oxo, methyl ester (90%)	Levulinic acid	Keto acid
3	12.820	Butanedioic acid, dimethyl ester (90%)	Succinic acid	Dicarboxylic acid
4	16.517	Dimethyl-dl-malate (83%)	Malic acid	Dicarboxylic acid
5	19.234	Thiophene, 3–4-diethyl (86%)	Thiofuran	Heterocyclic aromatics
6	20.270	2-Furancarboxaldehyde, 5-hydroxymethyl) (95%)	Hydroxymethylfurfural	Furans
7	36.087	2-Propenoic acid, 2-(4-hydroxyphenyl)-, methyl ester (93%)	p-Coumaric acid	Hydroxycinnamic acid
8	40.120	Hexadecenoic acid, methyl ester (Z) (99%)	Palmitoleic acid	Omega-7 monounsaturated fatty acid
9	44.609	9,12-Octadecadienoic acid (Z,Z), methyl ester (99%)	Linoleic acid	Omega-6 fatty acid (essential)
10	44.756	9-Ocatdecenoic acid (Z), methyl ester (99%)	Oleic acid	Monounsaturated omega-9 fatty acid
11	45.344	Octadecanoic acid, methyl ester (99%)	Stearic acid	Saturated fatty acid
12	49.650	Eicosanoic acid, methyl ester (99%)	Arachidic acid	Saturated fatty acid
13	53.62	Docosanoic acid, methyl ester (98%)	Behenic acid	Saturated fatty acid
14	57.317	Tetracosanoic acid, methyl ester (99%)	Lignoceric acid	Saturated fatty acid
(d) Radisl	h peel			
1	4.978	Furfural (91%)	Furan-2-carboxaldehyde	Heterocyclic aldehyde
2	8.577	Propanedioic acid, dimethyl ester (90%)	Malonic acid	Dicarboxylic acid
3	12.834	Butanedioic acid, dimethyl ester (90%)	Succinic acid	Dicarboxylic acid
4	16.517	Dimethyl-dl-malate (83%)	Malic acid	Dicarboxylic acid
5	40.66	Hexadecanoic acid, methyl ester (98%)	Palmitoleic acid	Omega-7 monounsaturated fatty acid
6	44.602	9,12-Octadecadienoic acid, methyl ester (98%)	Linolelaidic acid	Omega-6 trans fatty acid
7	44.749	9,12,15-Octadecatrienoic acid, methyl ester, (Z,Z,Z)- (99%)	α-Linoleic acid	Omega-3 fatty acid (essential)
8	44.875	9-Octadecenoic acid (Z)-methyl ester (98%)	Oleic acid	Monounsaturated omega-9 fatty acid

Rt, retention time

Data in parenthesis indicate the per cent similarity of the compound to the existing database that was used to identify the compound

dicarboxylic acid (malonic acid) with furan (hydroxymethylfurfural) and (un)saturated fatty acids (tridecylic acid, palmitic acid and oleic acid). In date seed extracts, the six constituents represented furfural, hydroxymethylfurfural and saturated fatty acids (lauric, myristic, palmitic and linolelaidic acid). Fourteen compounds were identified in pineapple skin, which belonged to the class: 1. dicarboxylic acid (oxalic, succinic and malic acid). 2. keto acid (levulinic acid), 3. aromatics (Thiofuran), 4. furan (Hydroxymethylfurfural), 5. hydroxycinnamic acid (p-coumaric

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 Table 4
 Elemental composition of the polyphenol and essential fatty acid-rich food wastes

Element	Pineapple skin	Onion peel	Radish peel
N (mg/g)	12.8±1.1	3.4±1.1	39.9±1.5
P (mg/g)	0.1 ± 1.4	0.2 ± 1.6	6.9±1.6
K (mg/g)	0.5 ± 1.9	2.5 ± 1.8	39.6 ± 1.2
Ca (mg/g)	2.2 ± 1.9	12.9 ± 1.2	5.5 ± 1.2
Mg (mg/g)	0.7 ± 3.2	2.8 ± 2.3	2.6 ± 1.5
S (mg/g)	0.6 ± 1.1	0.9 ± 1.2	6.9±1.1
Mn (μg/g)	9.5 ± 0.2	59.3 ± 2.3	25.1 ± 2.2
Fe (µg/g)	604.3 ± 3.2	27.0 ± 2.0	477.1 ± 5.1
Ni (µg/g)	1.9 ± 0.9	0.03 ± 1.0	1.9 ± 0.5
Co (µg/g)	0.3 ± 1.7	BDL	0.5 ± 1.0

Values are means \pm standard deviation (n = 3)

BDL, below detection limit of ICP–MS (Co=0.1 μ g/L)

acid), 6. monounsaturated omega (palmitoleic and oleic acid), polyunsaturated omega-6 (linoleic acid) and saturated (stearic, archidic, behenic and lignoceric acid) fatty acids. One of the significant features is GC–MS analysis of the radish peel methanol extracts revealed that it is the major constituent of alpha-linoleic acid which is essential for humans and other animals [55, 56]. With alpha-linoleic acid being the prime source, radish peel also constituted furfural, malonic acid, succinic acid, malic acid and unsaturated omega fatty acids like palmitoleic acid, linolelaidic acid and oleic acid.

ICP–MS analysis revealed that the high polyphenol and essential fatty acid constituting skins of onion, pineapple and radish are rich in essential micro- and macronutrients (Table 4). Pineapple skin and radish peel being the richest source of Fe. Notably, radish peel comprised a relatively higher level of essential elements than the other two showing its potential as a superior food waste which can be even used as an soil amendment or in compositing or as an substrate to develop nanofertilizer because of its reducing potential and chemical significance.

According to the obtained results, it is obvious that the peels from onion, pineapple and radish are not a waste, but a resource containing essential compounds and hence can be harnessed for food and pharmaceutical applications. Though a brief discussion of the food wastes oil extracts (for example, onion skin) for their chemical composition had been reported [57], a cumulative overview of the phytochemical profile of the predominant compounds of original food wastes as detailed in the current study is of significance. Our result on chemical profiling of date seed is in agreement with some other studies [58, 59] except where presence of furfural and linolelaidic acid is observed for the first time in this study.

4 Conclusion

This study provides new knowledge on the phytochemical properties and range for all the food waste classes employed and assists in identifying the most resourceful wastes. These new data are valuable additions to the database for the food processing, pharmaceutical, remedial and fertilizer industries and represent a significant step towards efficient waste management and economic return as value-added products. They will also assist to combat environmental threats via a green synthesis of nanoparticles and bioadsorbents against the pollutants. We recommend extracting, measuring and identifying the useful bioactive compounds of fruit and vegetable wastes. The screening of individual polyphenol constituents that exhibit health-promoting properties in onion peel, radish peel, pineapple skin and date seed requires further investigation.

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Compliance with ethical standard

Conflict of interest The authors declare that they have no conflict of interest.

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