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FOOD INDUSTRY WASTE: MINE OF NUTRACEUTICALS

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Abstract: Waste utilization from food processing industries is highly indispensable and challenging task all around the globe. Generation of this waste is inevitable because every time we have to produce the finished product of the same consistency without taking into consideration the amount of waste produced. Numerous researchers have worked on generation of phytochemicals, antioxidants, dietary fibre, food ingredients like pectin, natural colour, vitamins, antibiotics and proteases apart from ethanol or biogas from waste generated from fruits, vegetables, cereals, pulses milling, coffee processing units. This paper is an attempt to collate the work done on the waste treatment from fruits, vegetables, cereals, pulses, coffee and arable crops for production of useful ingredients followed by case studies of major individual fruits, apple, mango, pineapple and grapes.

Introduction

About 18 per cent of the fruit and vegetables production worth Rs. 44,000 crore is going waste annually in India (2012 data). The level of fruits and vegetable processing is dismally 4%. While only 20% of fruits and vegetables are exported, most of our production is for caters to the defence, institutional sectors and household consumption. Also the fruit and vegetable processing industry in India is highly decentralized. A large number of units are in the cottage/home scale and small scale sector, having small capacities upto 250 tonnes/annum. The big Indian and multinational companies in the sector have large capacities in the range of 30 tonnes per hour or so.

When we think of the practical implications of utilization of waste from this sector, these statistics need to be taken into account. For any profitable waste treatment facility, there needs to be segregated waste from a single fruit or vegetable so that it may be treated accordingly for generation of various pharmaceutical, nutraceutical or food ingredient. Thus a cluster type approach for fruits and vegetables processing would ensure generation of waste

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of uniform composition and quality such that bulk handling may be done to generate useful ingredients from them.

Fruits and vegetables comprise of carbohydrates like sugars, dietary and resistant fibres; vitamins and minerals. Waste by definition means anything unused or not used to full advantage. When fruits and vegetables are consumed for household purposes, waste might mean any rotten or over/under-ripe fruit or vegetable. While in fruits or vegetables processing sector, the composition of waste is different, i.e., it will contain less of over or under-ripe fruit or vegetable, rotten organic matter but more of cellulosic waste like peels and seeds. The use of this composite mass of cellulosic or fibrous waste with some carbohydrates is seen as a mine of phytochemicals by most researchers.

The full utilization of horticultural produce is a requirement and a demand that needs to be met by countries wishing to implement low-waste technology in their agribusiness. The waste obtained from fruit processing industry is extremely diverse due to the use of wide variety of fruits and vegetables, the broad range of processes and the multiplicity of the product. Vegetables and some fruits yield between 25% and 30% of non-edible products.

Dependingon plant species, variety and tissue, high levels of health protecting antioxidants, such as vitamin C and E, phenolic compounds including phenyl-propanoids and flavonoids, and or carotenoids such as lycopene can be found. The waste materials such as peels, seeds and stones produced by the fruit and vegetable processing can be successfully used as a source of phytochemicals and antioxidants (Table 1). The entire tissue of fruits and vegetables is rich in bioactive compounds, such as phenolic compounds, carotenoids, vitamins and in most cases, the wasted by products can present similar or even higher contents of antioxidant and antimicrobial compounds than the final produce can. The new aspects concerning the use of these wastes as by-products for further exploitation on the production of food additives or supplements with high nutritional value have gained increasing interest because these are high value products and their recovery may be economically attractive. The by-products represent an important source of sugars, minerals, organic acid, dietary fibre and phenolics which have a wide range of action which includes anti-tumoral, antiviral, antibacterial, cardio protective and antimutagenic activities. Utilisation of by-products is, however, limited due to the poor understanding of the irnutritional and economic value.

The extent of the waste produced and available from processing industries of some of the important fruits and vegetables, is given in Table 2.

The most abundant by-products of minimal processing of fresh-cut fruit and vegetable are peel and seed and those are reported to contain high amounts of phenolic compounds with antioxidant and antimicrobial properties. The brief discussion of major ingredients of industrial importance obtained from fruits and vegetables waste follows.

A. Phytochemicals and Phytoceuticals

Nowadays, there is a growing interest in finding phytochemicals as an alternative to synthetic substances, which are commonly used in the food, pharmaceutical and cosmetic industry.

Some interesting facts:

Several studies have shown that the content of phytochemical compounds is higher in peel and seeds with respect to the edible tissue. The total phenolics and flavonoid contents were higher in the by-products as compared to the final products, being more pronounced in mango seeds and peels.

- Gorinstein*et al*., (2001) found that the total phenolic compounds in the peels of lemons, oranges, and grapefruits were 15% higher than that of the pulp of these fruits.
- Peels from apples, peaches, pears as well as yellow and white flesh nectarines were found to contain twice the amount of total phenolic compounds as that contained in fruit pulp. Apple peels were found to contain up to 3300 mg/100 g of dry weight of phenolic compounds.
- While the edible pulp of bananas (*Musa paradisiaca*) contains 232 mg/100 g of dry weight. phenolic compounds, this amount is about 25% of that present in the peel (Someya *et al*., 2002).
- Pomegranate peels contain 249.4 mg/g of phenolic compounds as compared to only 24.4 mg/g phenolic compounds found in the pulp of pomegranates.
- Total phenolic compounds of seeds of several fruits, such as mangos, longans, avocados, and jackfruits, were higher than that of the edible product,
- Grape seeds and skins, the byproducts of grape juice and white wine production, are also sources of several phenolic compounds, particularly mono, oligo, and polymeric proanthocyanidins (Shrikhande, 2000).
- The peels and seeds of tomatoes are richer sources of phenolic compounds than the pulp of the tomatoes are.
- The peel byproduct of tomato has significantly higher levels of total phenolic compounds, total flavonoids, lycopene, ascorbic acid, and antioxidant activity as compared with the pulp and seeds (George *et al*., 2004).

B. Dietary fibre

Dietary fibre plays an important role in the prevention and cure of diabetes, obesity, atherosclerosis, heart diseases, colon cancer and colorectal cancer. Hemicellulose and pectin were found to have a remarkable capability of binding metal ions. The utilization by-products or wastes from industrial processing of fruit and vegetables, i.e. apple, currant, citrus fruit, carrot, tomato, melon or spinach pomace is convenient and cost-effective and enables rational management of trouble some wastes.

Investigations into fruit and vegetable pomace have revealed a neutral dietary fibre (NDF) content of 18 to 87%DM, and an Acid dietary fibre (ADF) content ranging between 16 and 57% DM. The NDF content in the fruit pomace varies from 24.20 g/100 g DM to 87.48g/100 g DM, and that in the vegetable pomace from 18.05 g/100 g DM to 34.76 g/100 gDM. The ADF content is very high in the fruit pomace (19.81 to 57.24 g/100 g DM) and slightly lower in the vegetable pomace (16.02 g/100 g DM to 29.33 g/100 g DM). Statistical analysis of theADF content has revealed seven homogeneous groups. The pomace from chokeberry, red cabbage and 'Dolanka' carrot pressing has formed independent homogeneous groups. Black currant pomace and 'Kent' strawberry pomace belong to the same single group. The pomace from both types of strawberries and that from both types of apples have formed two separate groups; the last of the homogeneous groups being made of 'Black' carrot and 'Champion' apples. Chokeberry pomace was found very rich in dietary fibre, containing the highest amounts of NDF (87.49 g/100 g DM) and ADF (57.24g/100 g DM). They also show the highest content of cellulose (34.56 g/100 g DM) and hemicellulose (30.24 g/100 g DM).

Compared to the majority of fruit pomace samples, the vegetable pomace samples showed slightly lower contents of particular DF fractions. The DF content was higher in the red cabbage pomace samples than in the pomace samples of 'Black' and 'Dolanka' carrots (NDF: 34.76 g/100 g DM; ADF: 29.33 g/100 g DM); cellulose and hemicellulose content amounting to 15.20 g/100 g DM and 14.13 g/100 g DM, respectively. Carrot pomace ('Black' and 'Dolanka' carrots) showed the lowest DF content. Their characteristic feature was a very low amount of hemicellulose (2.03 and 4.98 g/100 g DM), similar amounts being determined in the 'Idared' apple pomace (4.26 g/100 g DM). 'Black' carrot (as well as 'Black' carrot pomace) is rich in anthocyanins and should therefore be recommended as a valuable raw material for functional food production, in spite of the rather low DF content.

C. Polysaccharides

Polysaccharides extracted from mulberry leafs, show anti-oxidant properties (tested as DPPH-scavenging activity) and good anti-bacterial effects against some common pathogens such as *B. subtilis*, *E. coli* and *S. Aureus* (Wang & Jiang, 2010). High molecular weight polysaccharides from *Opuntiaficus-indica* accelerating re-epithelizationina model of dermal wound (Trombetta et al., 2006) or those from *Salvia chinensis* eliciting B-lymphocytes *in vivo* (Liu et al., 2002) or even some pectic polysaccharides from ginseng that are able to rescue cell viability from rotavirus infection. Finally, polysaccharides extracted from plants such as *Aloe barbadensis Miller, Lentinusedodes, Ganodermalucidum, Coriolusversicolor*, resulted to exert both anti-genotoxic and anti-tumor promoting activities *in vitro* models and thus might be considered as potential cancer hemo-preventive substances (Hyung et al., 1999).

Natural polymers have been suggested for tissue engineering also. The well-known self-assembly capabilities and stimuli responsiveness of polysaccharides make them suitable bio-materials for different applications in fields like biodegradable plastic production, nano-material science and the already discussed bio-compatible materials production for medical uses. Polysaccharides are used with or without chemical modifications that have been the object of several researches in order to obtain new biodegradable and sustainable materials. Starch has been extensively exploited for the realisation of biodegradable plastic and resins that can be blown into film, injection moulded and thermoformed; it is also fermented to lactic acid producing polylactic acid polymers and co-polymers employed for biodegradable plastic production (Narayan, 1994).

In addition, it is currently object of massive research efforts for the production of the so-called thermoplastic starch and the processing of foamed materials for loose-fill packaging (Gandini, 2008). Cellulose from wood pulp is mostly used for the production of paper and cardboard and the regeneration of fibres and films (for coatings, laminates, optical films), as well as for building materials, pharmaceuticals, foodstuffs, and cosmetics (Klemm et al., 2005); microfibrils are also employed in nano-material science for manufacturing nano-paper or as reinforcing elements in composite materials; cellulose whiskers have been used as mechanical reinforcing agents for low-thickness polymer electrolytes for lithium battery applications.

Starch, cellulose and pectin have been together also the subject of intense research to assess their use as electro active polymers. These latter are a new class of materials that can be potentially used for several applications as biosensors, environmentally sensitive membranes, artificial muscles, solar materials, *etc.* (Finkenstadt, 2005).

Pectin

India is producing 3 million tonnes of citrus fruits like mandarins, lime, lemon, and sweet orange. Citrus wastes are rich source of oil, pectin and variety of by-products. The failure or inability to salvage and reuse such materials economically results in the unnecessary waste and depletion of natural resources. Apple and citrus wastes are traditionally the main sources of commercial pectin (Thibault & Ralet, 2003). They are generated from processing industries for apple and citrus fruits afterjuice extraction that are among the foremost food industries, Pectins are industrially obtained from apple pomace and citruspeels by means of acid extraction (i.e. oxalic, hydrochloric, nitric and sulphuric acid) at high temperatures (80-90°C).

Besides pectin, other main components of apple pomace are the cell wall polysaccharides cellulose and xyloglucan. Recent investigations were focused on the pomacexyloglucan component that was isolated by means of alkaline extraction and was identified as a fucogalacto-xyloglucan. Such xyloglucan (after derivatisation procedures similar to cellulose conversion into methylcellulose, hydroxypropylcellulose, carboxymethyl cellulose) might be useful as thickening agent, texture modifier or as a source of biologically active oligosaccharides (Watt et al., 1999).

Citrus fruits are particularly rich in pectin (ranging from 20 to 30% of dry matter waste) and the large quantities of citrus wastes generated by the fruit juice industry represent one of the most important raw material for the production of commercial pectin. Several varieties of citrus fruits (including lemon, lime, orange and grapefruit) have been investigated aspolysaccharides sources and different extraction techniques have been tested. The yields and quality of the pectins extracted can be improved by means of pretreatment with microwaves as shown by studies carried out on orange peels. Microwaves are able to destroy the plant tissue thus increasing the porosity and the water absorption capacity of the plant material that results in a considerable increase in the yield of extractable pectin and improvement of its parameters (e.g. degree of esterification, molecular mass and gel strength) (Kratchanova et al., 2004).

Another interesting example of citrus waste biomass is represented by bergamot, *Citrus bergamia* Risso, residues: bergamot is used in Italy mostly for the extraction of its essential oil, obtained by wash-scraping the fruit. The annual Italian production of bergamot amounts to 25,000 tons and peel is an under-utilized by-product of the essential oil and juice processing industry that likewise other citrus waste peels still contain sexploitable biopolymers such as pectins. A sequential ethanol/water extraction has been used and it afforded 29.8% polysaccharide's yield in the 70% ethanol soluble fraction and a 45.2% yield in the alcohol insoluble fraction. Chemical analysis of the isolated fractions showed that both of them were mainly composed of pectic substances encasing the cellulose microfibrils (Mandalari et al., 2006).

D. Bioethanol

The rising global energy requirements together with the depletion of fossil fuel reserves have highlighted the importance of developing technologies to exploit renewable energy sources and for clean carbon-neutral fuel productions, i.e. biofuels. Polysaccharides are renewable sources of monomer sugars to ferment for the production of bioethanol, one of the most used biofuel in the world. Starch from corn is nowadays one of the main sources of bioethanol, although also cellulosic biomasses are under investigation because they could allow ethanol production without displacing agricultural food crops like corn. Nevertheless, biological transformation of cellulose to ethanol is a technology still under investigation because of the harsh conditions required for the industrial process that make it still far from being efficient and costly effective.

Biological properties of polysaccharides from tomato, granadilla and lemon wastes

The anticytotoxic activity of polysaccharides as function of inhibition of Avarol (10 µg/ml) toxicity in brine shrimp (*Artemiasalina*) bioassay was evaluated by Minale et al., 1974. Avarol (a natural toxic sesquiterpene hydroquinone isolated from *Dysideaavara* sponge) shows strong toxicity (LC50 0.18 µg/ml) in brine shrimp bioassay, that gives results well correlated with cytotoxicity in the cancer cell lines such as KB, P388, L5178y and L1210 (De Rosa et al., 1994). For this assay 10 ppm Avarol were used in order to obtain the death of all the brineshrimp larvae. The biopolymer isolated from granadilla and lemon peels was found to be an anti-cytotoxic compoundin this bioassay, increasing the value of Avarol LD_{50} from 0.18 µg/ml up to 2.13 µg/ml when present at a concentration of 500 ppm. Thus suggesting a role for this biopolymer in the control of oxidative stress and/or inflammation process.

E. Biofilms

Another useful application of polysaccharides extracted from tomato processing industrial wastes and from granadilla peels is the development of **biodegradable films** by means of biopolymers and glycerol solutions (Strazzullo et al., 2003; Tommonaro et al., 2007).

Applying the procedure previously described, solid, clear and elastic films were obtained from both polysaccharides, able to recover small deformations produced by tensilestress applied. These biofilms could have interesting biotechnological applications indifferent fields, such as agriculture, e.g. for protecting cultivations with mulching operation techniques. In the case of polysaccharide extracted from lemon pomace, no results were obtained using the same procedure for biofilm production and, therefore, further studies are needed.

F. Proteases

Wastes like potato, pumpkin, cauliflower, cabbage and brinjal have been employed for production of protease by solid state fermentation using *Aspergillusniger.* Estimation of specific activities for individual substrates conferred the highest upon pumpkinwith13.44 U mg protein/ml, with comparable results obtained for cauliflower and cabbage. This study presents a novel - economical approach for the bioconversion of vegetable wastes for the production of protease that is industrially significant.

G. Single cell Proteins

Mondel et al. (2012) investigated the production of *Saccaharomycescerevisiae* in cucumber and orange peels and found that higher amount of crude protein (53.4%) was obtained from cucumber peels. Cucumber peels contained higher amount of available carbohydrates and minerals which might have favorably affected yeast biomass production. Though orange peel also contained high concentration of carbohydrates but supported less biomass production. This may be due to the less mineral content in orange peels (3.55%) than that of in cucumber peels (6.96%) and hence resulted in lower growth of yeast biomass.

CASE STUDIES

Mango

India ranks first among world's mango producing countries accounting for about 40% of the world's mango production (12.3 MT). Global production of mangoes was about 30.7 million tonnes by 2010 and the growth rate for this crop is 2.7%. Other major mango producing countries include China, Thailand, Mexico, Pakistan, Philippines, Indonesia, Brazil, Nigeria and Egypt. Processed mango products are among the major goods exported, hence, several million tons of mango seed wastes are produced annually from factories. There is approximately 13% seed in mangoes which nearly amount to 1.67 million tonnes of waste in India alone which has a high potential nutraceutical and food value.

India has over 250 varieties of mangoes of which major production is of 15 varieties for various purposes. Much of the work in this area has been done on Egyptian, Nigerian and Spanish mangoes. However, similar works on Indian varieties are lacking. Except for one or two works on the compositional details of Dussheri and Chausa, no know how is available on the antioxidant and antimicrobial potential of Indian mango varieties.

Mango seed kernel composition

Mango seed kernels have been found to contain a considerable amount of total phenolic compounds, total lipid, unsaponifiable matter, and a low amount of crude protein, but the quality of protein was good because it was rich in all essential amino acids. Proximate composition, amino acid profile and antinutrients contents of Nigerian mango seed were investigated. Mango seed contains 10.06% crude protein, 14.80% oil, 2.62% ash, 2.40% crude fibre, 70.12 % carbohydrate and energy content 453.92 KJ/100 g. Mango seed is very rich in glutamate (13.00 g/100 g of protein) while methionine has the lowest value (1.04 g/100 g of protein).

Antioxidant Properties

Addition of 400 ppm methanol extract and 5% mango seed kernel oil could increase the oxidative stability of sunflower oil incubated at ambient temperature as well as sunflower oil during frying. Moreover, both extract and oil improved the stability and quality characteristics of fresh and stored potato chips. These results provide useful information on the utilization of mango seed kernel as natural antioxidant in foods. Thai Mango seed kernel has been shown to be a good source of phenolic antioxidants, metal chelators and tyrosinase inhibitors. 1,2,3,4,6-Penta-O-galloyl-beta-D-glucopyranose, methyl gallate and gallic acid have been identified as components of an ethanolic extract of Thai mango seed kernel cultivar Fahlun. In Nigerian mango variety Ikanekpo, the level of tannin (45 g kg^{-1}) was high and 48% could be extracted by a combined soaking and thermal treatment employed during flour production.

Presence of at least six phenolic compounds and eight phospholipids in the isolates has been confirmed by chromatographic techniques. Phenolics and phospholipids isolated from mango seed kernel, when added jointly to buffalo ghee, helps in extending the shelf-life of ghee. Mango seed extract at 0.1 or 0.2% levels in Bologna-type mortadella has better antioxidant activity than BHT in reducing colour loss and lipid oxidation.

Mango seed extracts from certain Thai varieties showed strong antioxidant activities against both $ABTS^{\cdot+}$ and $DPPH^{\cdot}$ radicals. In some varieties antiradical activity was even stronger than vitamin C, trolox, as well as a synthetic antioxidant compound, BHA. All seed extracts inhibit growth of both gram negative and gram positive bacteria. The most sensitive strain found was the opportunistic gram negative bacteria, *Ps. Aeruginosa* (ATCC 27853). Hepato protective properties of the mango kernel extract (MKP) have been reported by determining their *in vitro* anti-inflammatory activities, and by evaluating their hepato protective potential against liver injury in rats induced by carbon tetrachloride (CCl_4).

During processing of mango, peel is a major by-product. Peel contributes about 15-20% of the fruit. Peel is not currently utilized for any commercial purpose and is discarded as a waste pollution. The mango peel (MPP) has been found to be phytochemicals, such as polyphenols, carotenoids, vitamin E, dietary fibre and vitamin C good antioxidant properties (Table 3). The whole fruit weight, depending on the mango variety the 45% to 75% of the whole seed. Seed represents from 20% to 60%.

The antioxidant and tyrosinase inhibitory properties of extracts of mango seed kernel (*Mangiferaindica* L.), have also been studied. Extracts contained phenolic components by a high antioxidant activity, which was assessed in homogeneous solution by the 2,2-diphenyl-1-picrylhydrazyl radical and 2,2′-azinobis (3-ethylbenzothialozinesulfonic acid) radical cation-scavenging assays and in an emulsion with the ferric thiocyanate test. The extracts also possessed tyrosinase inhibitory activity. Drying conditions and extraction solvent were varied, and optimum conditions for preparation of mango seed kernel extract were found to be sun-drying with ethanol extraction at room temperature. Refluxing in acidified ethanol gave an increase in yield and the obtained extract had the highest content of total phenolics, and also was the most effective antioxidant with the highest radical-scavenging, metal-chelating and tyrosinase inhibitory activity. The extracts did not cause acute irritation of rabbit skins. Our study for the first time reveals the high total phenol content, radical-scavenging, metal-chelating and tyrosinase inhibitory activities of the extract from mango seed kernel. This extract may be suitable for use in food, cosmetic, nutraceutical and pharmaceutical applications.

Mango seed kernel composition

Mango seed kernels have been found to contain a considerable amount of total phenolic compounds, total lipid, unsaponifiable matter, and a low amount of crude protein, but the quality of protein was good because it was rich in all essential amino acids. Proximate composition, amino acid profile and antinutrients contents of Nigerian mango seed have been investigated. Mango seed contains 10.06% crude protein, 14.80% oil, 2.62% ash, 2.40%

crude fibre, 70.12 % carbohydrate and energy content 453.92 KJ/100 g. Mango seed is very rich in glutamate (13.00 g/100 g of protein) while methionine has the lowest value (1.04 g/100 g of protein).

Antioxidant Properties

Eight phenolic compounds have been identified in mango seed extract amongst which tannin and vanillin were in highest amounts. The same group investigated both mango seed kernel extract and its oil for their antioxidant potency and antimicrobial effect. Addition of 400 ppm methanol extract and 5% mango seed kernel oil could increase the oxidative stability of sunflower oil incubated at ambient temperature as well as sunflower oil during frying. Moreover, both extract and oil improved the stability and quality characteristics of fresh and stored potato chips. These results provide useful information on the utilization of mango seed kernel as natural antioxidant in foods. Thai Mango seed kernel has been shown to be a good source of phenolic antioxidants, metal chelators and tyrosinase inhibitors. In addition, phenolic compounds in 11 cultivars of Thai mango seed kernels. 1,2,3,4,6-Penta-O-galloyl-beta-D-glucopyranose, methyl gallate and gallic acid have been identified as components of an ethanolic extract of Thai mango seed kernel cultivar. In Nigerian mango variety Ikanekpo, the level of tannin (45 g kg^{-1}) was high and 48% could be extracted by a combined soaking and thermal treatment employed during flour production.

Results have demonstrated that the phenolics and phospholipids isolated from mango seed kernel, when added jointly to buffalo ghee, helped in extending the shelf-life of ghee. Mango seed extract was used at 0.1 or 0.2% levels in Bologna-type mortadella as antioxidant and compared its activity with BHT at 0.01% and found its better antioxidant activity in reducing colour loss and lipid oxidation.

Mango seed extracts from certain Thai varieties showed strong antioxidant activities against both $ABTS^{\cdot+}$ and $DPPH^{\cdot}$ radicals. In some varieties antiradical activity was even stronger than vitamin C, trolox, as well as a synthetic antioxidant compound, BHA. All seed extracts inhibit growth of both gram negative and gram positive bacteria. The most sensitive strain found was the opportunistic gram negative bacteria, *Ps. Aeruginosa* (ATCC 27853). Hepatoprotective properties of the mango kernel extract have been reported by determining their *in vitro* anti-inflammatory activities, and by evaluating their hepatoprotective potential against liver injury in rats induced by carbon tetrachloride (CCl_4). The hepatoprotective effect of MSKE is clearly supported by its polyphenolic nature of the main principle, PGG, which exhibited potent antioxidant and anti-inflammatory activities.

Antimicrobial Properties

Antimicrobial substrates are potentially useful as food additives to extend the shelf-life of foods, in particular unheated products such as beverages where heat treatment may impair their delicate flavor profile. Because the mango kernel extract (MKE) has heat and pH stability, it can be applied in a variety of foods.

The minimum inhibitory concentrations of the MKE against *Campylobacter jejuni* and *Yersinia enterocolitica*, were 100 and 50 ppm, while those of the crude catechins from green tea and the aflavins from brown teas are greater than 1000 ppm suggesting its better efficacy as compared to other natural antimicrobials. The antimicrobial spectrum of the MKE was found more effective against gram-positive bacteria than gram-negative bacteria, although the antimicrobial activity against lactic acid bacteria was ineffective.

Mango seed kernel extract was found to reduce total bacterial count, inhibited coliforms growth, showed remarkable antimicrobial activity against *Escherichia coli* strain and extended the shelf-life of pasteurized cow milk .Starches separated from kernels of five different Indian mango cultivars (Chausa, Totapuri, Kuppi, Langra and Dashehari) have been investigated for physicochemical, morphological, thermal and rheological properties.

Apple

Applepomace is the by-product of processing for the recovery of apple juice and amounts to up to 25–35% of the processed fruit. It is a rich source of polyphenols, minerals and dietary fibre. Although it is conventionally used as an animal feed, the production of pectin is considered to be the most reasonable utilization approach from both economical and ecological points of view. Pectin consists of 10–15% of apple pomace, on a dry weight basis and is recovered by acid extraction and precipitation. Pectin currently produced from apple pomace has more superior gelling properties than citrus pectin but presents a brown hue that may limit its incorporation into light-colour foods.

The colour of apple pomace and extracted pectin is formed by the oxidation of phenolic constituents that are co-extracted with pectin and partially precipitated. Apple pomace has been shown to be a good source of polyphenols which are predominantly localized in the peels and are extracted into the juice to a minor extent. Major compounds isolated and identified include catechins, hydroxycinnamates, phloretin glycosides, quercetin glycosides, and procyanidins.

Apple pomace contains polyphenols like epicatechin, its dimer (procyanidin B2), trimer, tetramer and oligomer, quercetinglycosides, chlorogenic acid, phloridzin and 3-hydroxyphloridzin. All the compounds showed strongantioxidant activities, and their DPPH-scavenging activities were 2-3 times and superoxide anion radical--scavenging activities were 10-30 times better than those of the antioxidant vitamins C and E. The antiradical activity of apple pomace was tested by measuringtheir ability to scavenge DPPH and hydroxylradicals by ESR spectroscopy. The highest DPPH(EC DPPH50 = 6.33 mg/ml) and hydroxyl (EC OH 50 = 26.11mg/ml) radical scavenging activities were obtained in the case of Reinderspomace. The total phenolics, total flavonoids, total flavan-3-ols, and some individual phenolic compounds contributed significantly to the antiradical activities of apple pomace. Furthermore, tumour-cell proliferation has strongly inhibited in vitro by apple extracts, and these effects have been attributed to phenolic acids and flavonoids. The phenolic components of apples have been linked with the inhibition of colon cancer in vitro. Apple extracts (both with and without skin) were found to inhibit the proliferation ofCaCo-2 cells in a dose-dependent manner, the inhibitoryeffect was greater in extracts containing apple skins. A flavonoid mixture from apples inhibited the proliferation of HT-29 (colonadenocarcinoma) cells.

Grape

Grapes (Vitis sp., Vitaceae) pomace represents approximately 20% of the weight of grapes. Its composition varies considerably, depending on grape variety and technology of wine making. However, wine making leads to the generation of large quantities of wastes (around 5–9 million tonnesper year, worldwide), which considerably increase the chemical oxygen demand (COD) and the biochemicaloxygen demand (BOD) due to a high pollution load Grape pomace is considered as a valuable source of phenolic compounds which could be recovered as functional food ingredients.

The seeds constitute a considerable proportion of the pomace, amounting to 38–52% on a dry matter basis. Their oil is rich in unsaturated fatty acids, linoleicacid in particular. Grape seed oil is mainly produced in Italy, France and Spain; however, the demand for this oil has also increased in the rest of Europe. Apart from being a rich source of high-value fatty oil, grape seeds have also been appreciated because of their content of phenolic compounds such as gallic acid, catechin and epicatechin, and a wide variety of procyanidins.

Thus, fractionation, isolation, and structural identification of grape seed proanthocyanidins have been extensively studied. Only procyanidin-type of proanthocyanidins, with partial galloylation, was detected in grape seeds. The degree of polymerization maybe reached around 30. Several individual dimerandtrimerprocyanidins were successfully isolated from grape seeds. Also, a great range of products such as ethanol, tartrates, citric acid, grape seed oil, hydrocolloids, and dietary fibre are recovered from grape pomace. Anthocyanins have been considered the most valuable components, and methods for their extraction have been reported in literature. Catechin, epicatechin, epicatechingallate and epigallocatechin were the major constitutive units of grape skin tannins.

The antioxidant activity of the extracts obtained from grape by-products was analyzed by different in vitro tests: scavenging of the stable DPPH radical, reactive OH, O^{2-} and of authentic peroxynitrite (ONOO-). Catechin and epicatechin in seeds and quercetin, rutin and resveratrol in skin extracts possess strong antiradical activity. Quercetin, catechin and epicatechin showed maximum activity.

Recent reports indicate a wide range of biological activities, e.g. radio protective effects, the prevention of cataract, anti-hyperglycemic effects, the enhancement of postprandial lipemia, the modulation of the expression of antioxidant enzyme systems, the inhibition of the protein kinease activity of the epidermal growth factor receptor, protective effects against oxidative damage in mouse brain cells, and anti-inflammatory effects. The high efficiency of natural phenolic extracts obtained from grape seeds as potent antioxidants was confirmed, by the fact which encourages the prospect of their commercialization as natural powerful antioxidantsin foods in order to increase the shelf life of food by preventing lipid peroxidation and protecting from oxidative damage. Many of the grape seed products are commercially available.

Citrus fruits

Citrus is the largest fruit crop worldwide, with approximately 100 million metric tons produced annually. The family of citrus fruits consists of Oranges, Kinnow, Khatta, Lime, Lemon, Grapefruit, Malta, Sweet orange etc. The large quantities of processed citrus fruits result in large amounts of by-products.

Citrus peel, remaining after juice extraction, is the primary waste fraction amounting to almost 50% of the fruit mass. It is processed to dried pulp cattle feed and molasses, the latter being incorporated into the cattle feed or fermented for the production of valuable products like biogas, ethanol, citric acid, various enzymes, volatile flavouring compounds, fatty acids and microbial biomass. Pectin is also produced from the peel by acid extraction, dietary fibres by mechanical processing, while the recovery of flavonoids and carotenoids are new potential applications. The juice pulp from the finishing process and the essences recovered from the juice and the peel press liquor amounting to approximately 5% of the fruit mass, are also by-products that find industrial utilization. Citrus seeds amount to 0.1–5% of the fruit mass depending on the variety. They can be used for oil extraction and the recovery of terpenoids while the meal remaining from the extraction is a good source of proteins.

Citrus by-products, if utilized fully, could be major sources of phenolic compounds. The peels, in particular, are an abundant source of natural flavonoids, and contain higher amount of phenolics compared to the edible portions. It has been reported that the contents of total phenolics in peels of lemons, oranges, and grapefruit were 15% higher than those in the peeled fruits. The ability of a number of methods to extractphenolics compounds from citrus peels have been evaluated, such as γ-irradiation assisted extraction, solvent extraction, enzyme-assisted extraction, and heat treatment. However, these extraction methods have drawbacks to some degree. For example, γ-irradiation assisted extraction is still unknown to safety; solvent extraction has low efficiency and consuming time; heat treatment results in pyrolysis, and enzyme in enzyme-assisted extraction is easy to denature.

Flavonoids in citrus are a major class of secondary metabolites. The peel contains the highest amount of flavonoids than other parts and those flavonoids present in citrus fruits belong to six peculiar classes according to their structure. They are: flavones; flavanones; flavonols; is of lavones; anthocyanidins and flavanols.

Flavonoids from citrus that have been extensively studied for antioxidative, anti-cancer, anti-viral, and anti-inflammatory activities, effects on capillary fragility, and an observed inhibition of human platelet aggregation. Recent research suggests that citrus fruits possess another health benefit phytochemicals called limonoids, highly oxygenated triterpenoid. Citrus limonoidsappear in large amounts in citrus juice and citrustissues as water soluble limonoidglucosides or inseeds as water insoluble limonoidaglycones. The limonoidaglycones are responsible for the development of delayed bitterness in citrus and are converted to then on bitter limonoidglucosides during fruit maturation. Citrus fruits contain the limonoidslimonin, nomilinandnomilinic acid, while both neem seeds and leaves contain the limonoidazadirachtin.

Currently limonoids are under investigation for awide variety of therapeutic effects such as antiviral, antifungal, antibacterial, antineoplastic and antimalarial. Certainlimonoids are insecticides such as azadirachtin from the neem tree. Most recently several limonoidaglycones and a mixture of limonoidglucosides were administered in vitro to estrogen dependent and estrogen independent human breast cancer celllines.

Pineapple

It is anticipated that discarded fruit as well as the waste material can be utilized for further industrial processes like fermentation, bioactive component extraction, etc. In this regard, several efforts have been made in order to utilize pineapple wastes obtained from different sources. The wastes from pineapple canneries have been used as the substrate for bromelain, organic acids, ethanol, etc. since these are potential source of sugars, vitamins and growth factors. Several studies have been carried out since decades on trying to explore the possibility of using these wastes. In past, sugar has been obtained from pineapple effluent by ion exchange and further use it in syrup for canning pineapple slices.

Bromelain: Bromelain is probably the most valuable and the most studied component from the pineapple waste. It is a crude extract of pineapple that contains, among other components, various closely related proteinases, demonstrating, *in vitro* and *in vivo*, antiedematous, anti-inflammatory, antithrombotic, fibrinolytic activities and has potential as an anticancer agent. It is also used in food industry as meat tenderizer and as a dietary supplement. Crude commercial bromelain from pineapple stem has been purified by successive use of ion-exchange chromatography, gel filtration, and ammonium sulfate fractionation. Recently, purifications of bromelain from crude extract are reported using aqueous two-phase system and metal affinity membranes. Immobilization of stem bromelain via the lone histidine of metal affinity support had better thermal stability. Even without addition of preservatives, natural stability of fruit bromelain was retained to almost 80% when stored at -4 ^{o}C for 180 days.

Ethanol: Organisms like *Saccharomyces cerevisiae,* and *Zymomonasmobilis* ATCC 10988 were capable of producing about 8% ethanol from pineapple waste in 48 h after pretreating with enzymes cellulase and hemi-cellulase.

Phenolic antioxidant: Fruit phenolic content was found as 40.4 mg/100g as gallic acid equivalent with the highest ethyl acetate bound phenolic, 2.58 as chlorogenic acid equivalent, while juice had 358 mg/L as gallic acid equivalent.

Phenolic antioxidants from the wastes are also found to be in higher amounts. The methanol extraction yield and total phenolic contents of pineapple residue (pulp, seeds and peel) were 30.2% and 10 mg/g GAE. They co-related the antioxidant activities of the phenolic compounds using DPPH free radical scavenging activity and superoxide anion scavenging activity. Phenolic such as myricetin, salicyclic acid, tannic acid, *trans*-cinnamic acid and *p*-coumaric acid has been identified in the high dietary fiber powder form pineapple shell. The

FRAP value for pineapple peel has been reported as 2.01 mmol/100 g wet weight.

Potent fungicides from cinnamic, *p*-coumaric and ferulic acids have been produced from pineapple stems. Phenolic antioxidant from pineapple waste may be converted to more potent compounds by cytochrome P4502C9 is ozyme *invitro.* anti-inflammatory and anti-diabetic potential of pineapple stem waste. Our ongoing work on phytochemicals from pineapple peel and leaf showed a high antioxidant activity with high phenolic compounds. The leaf also has significant amount of phytosterol content, particularly beta-sitosterol, stigma sterola and campestrol.

Organic acids

Citric acid: It was found that solid state fermentation using *Aspergillusfoetidus* ACM 3996 produced higher amount of citric acid than from other waste sources such as apple pomace, rice or wheat brans. In one other report, researchers have used four species of *Aspergillus* to compare the production of citric acid under solid state fermentation. Under optimized conditions, a yield of 19.4 g citric acid/100 g dry fermented pineapple waste was obtained.

Lactic acid: Lactic acid has an important position in the family of carboxylic acids because of its application in both food and non-food industries. It is used as a preservative and acidulant in food industries. However, commercial production of lactic acid is costly due to the raw materials used (exploitation of biological waste). Fungal production of lactic acid from pineapple waste resulted in 19.3 and 14.7 g/L lactic acid with *Rhizopusarrhizus* and *R. oryzae*.

Ferulicacid: Ferulic acid is the most abundant hydroxyl cinnamic acid found in plat cell walls. This phenolic antioxidant is widely used in the food and cosmetic industry. Pineapple peel has been used for the alkali extraction of ferulic acid.

Energy and carbon source: Pineapple wastes generally comprise of organic substances and hence the disposal problem could be attenuated by anaerobic digestion and composting.

The sugars contained in pineapple cannery effluent have been utilized for the production of **single cell protein** using continuous cultivation. The dilution rate had significant effect on biomass as well as protein content. There was an increase in biomass and protein content of *Candida utilis* with increasing dilution rate.

***Anti-dyeing agent*:** Dyes used in textile industries have been a threat to environmental problem since these are visible in small quantities due to their brilliance when mixed and thrown with large volumes of waste water from different steps in the dyeing and finishing processes. Pineapple stem is used as low-cost adsorbent to remove basic dye (methylene blue) from aqueous solution by adsorption. In another report, pineapple leaf powder has been used as an unconventional bio-adsorbent of methylene blue from aqueous solution.

Fibre: Researchers have reported that dietary fibre powder prepared from pineapple shell has 70.6% total dietary fiber with better sensory properties than commercial dietary fibres from apple and citrus fruits.

Removal of heavy metals: Pineapple fruit residues have been used as an effective biosorbent to remove toxic metals like mercury, lead, cadmium, copper, zinc and nickel. They have reported that the addition of phosphate groups in the fruit residues increased the adsorbent capacities at lower pH. Reports on the removal of heavy metals like chromium, copper, lead, nickel and zinc from contaminated sewage sludge using citric acid obtained from fermented pineapple wastes with *A. niger* are found. The applicability of such contaminated sewage sludge after removal of heavy metals as land fill has shown to have high potentials. Pineapple waste water has also been used as cheap substitute of nutrients for *Acinetobacterhaemolyticus*, which was used to reduce the contamination of chromium VI.

By products from Cereals, Pulses and Oilseeds Processing

Rice husk and rice bran

Rice husk is the largest product of the rice milling industry comprising 20 to 25 per cent of paddy. Paddy yields about 5 to 7 per cent bran. The availability of rice husk is about 15 Mt annually. A typical paddy husk sample contains 42.6 per cent cellulose, 20.1 per cent Iignin, 18.6 per cent pentosans and 18.7 per cent ash. Rice bran yield is about 2.5 Mt annually. It is exploited for production of rice bran oil.

Coffee Industry By-products

Coffee production worldwide is approx. 105 million tons annually. Industrial processing of coffee is done by removing shell and mucilaginous part from cherries. Coffee is subjected to puling, washing, drying, curing, roasting, and brewing, and during the process, various by-products such as coffee pulp, cherry husk, parchment husk, silver skin and spent waste are obtained. Coffee pulp, husk, silver skin, and spent coffee were subjected to extraction of phenolics. Silver skin was found to have highest phenolics (25%), followed by spent waste (19%) and cherry husk (17%) after pre-treatment with viscozyme. The bioactive conserves prepared from coffee by-products possessed 65 to 70% antioxidant activity in terms of cholorogenic acid. The antioxidant activity of the by products was found to be 1.5 to 2.0 mmoltrolox/ 100g.

Pulse milling waste

Metal removal

Agro-waste basically composed of cellulose and lignin along with other components which carries a variety of functional groups having capability of complexing heavy metal ions which facilitate their removal by adsorption. The processing of agro-waste for their modification into carbon form is needed as in this form the agro-waste possesses high porosity and large surface area making it more effective for metal adsorption process.

Tur dal (*Cajanuscajan)* husk which is about 8 percent of the pulse grain and is the low cost by product or waste of pulse processing industry. The husk of tur dal is reported to contain about 5.6 percent crude protein, 0.3 percent fat, 31.9 percent crude fiber, 3.5 percent ash and 58.7 percent carbohydrates and possess potential to be used as metal adsorbent. Merely throwing Tur dal husk for cattle feed is the wasteful way of utilizing this material. The washed and dried tur dal husk was carbonized in air tight container at 500 ^{o}C for 1 hr. to get its carbon form possessing adsorption property.

SCP production

In a study, the Green gram and Bengal gram husk were used as a substrate for production of SCP in maltose enriched medium (7.7mg). It attained maximum yield of 9.2mg in 6-10days of fermentation. The minimum carbohydrate content was found in nitrogen enriched sources such as urea and peptone at early stages of fermentation but rapidly increased upto 54.4/ 100mg in 6-10days of fermentation. These changes indicated the utilization of carbon and nitrogen sources from pulse husk for production of biomass in fermentation medium.

Tannase production

Tannase is an extremely important in various industries such as in the manufacturer of instant tea, beer, fruit juice, coffee-flavour soft drink and grape wine. In addition, gallic acid, the product of hydrolytic cleavage of tannic acid, is a chemical used in pharmaceuticals. Immobilized tannase produced from *A.niger* fermented with Redgramhuk of biomass showed the highest activity of 45 U/g/min.

Summary

In conclusion, resources depletion and environmental concerns have triggered new regulations and growing awareness throughout the world, thus promoting the use of more and more fruit and vegetable waste to obtain by products with high functionality and health benefits. Accordingly, the production of useful biopolymers like polysaccharides starting from cheap and abundant renewable resources, such as residues of fruits and vegetables processed for food production, could contribute to the issue of waste management and to the recovery of valuable by products. The waste materials such as peels, seeds and stones produced by the fruit and vegetable processing can be successfully used as a source of phytochemicals and antioxidants. The new aspects concerning the use of these wastes as by-products for further exploitation on the production of food additives or supplements with high nutritional value have gained increasing interest because these are high value products and their recovery may be economically attractive. The by-products represent an important source of sugars, minerals, organic acid, dietary fibre and phenolics which have a wide range of action which includes anti-tumoral, antiviral, antibacterial, cardio protective and antimutagenic activities.

If effective utilization of food residues is to occur, food manufacturers should invest in specialized secondary industry to utilize the residues. Efforts are needed to develop new technologies and to institute suitable measures to promote waste reclamation; this can only be achieved if food residues are considered as complementary resources rather than as undesirable wastes. In any case, consumer protection must have priority over economic interests, and health claims need to be substantiated by standardized, scientifically sound and reliable studies.

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Table 1: Percentage of by-products generated during minimal processing of fruits

Fruit (minimally processed)	By-products generated
Sliced apples	10.91% of pulp and seed (core) by-products
Peeled mandarins	16.05% of peels
Diced papayas	6.51% of seeds, 8.47% of peels, 32.06% of unusable pulp (due to the lack of shape uniformity in a cube)
Pineapples	9.12% of core, 13.48% of peels, 14.49% of pulp, 14.87% of top
Mangoes	13.5% of seeds, 11% of peels, 17.94%. unusable pulp

Table 2: Fruits and vegetable wastes available in India

Commodity	Nature of waste	Production (content), tons	Approx. waste (%)	Potential quantities of waste, tons
Mango	Peel, stone	6987.7	45	3144.4
Banana	Peel	2378.0	35	832.3
Citrus	Peel, rag, seed	1211.9	50	606.0
Pineapple	Skin, core	75.7	33	24.7
Grapes	Stem, skin, seeds	565.0	20	-
Guavas	Peel, core and seeds	565.0	10	-
Peas	Shell	107.7	40	68.3
Tomato	Skin, core and seeds	464.5	20	90.3
Potato	Peel	2769.0	15	415.3
Onion	Outer leaves	1102.0	-	-
Apple	Peel, pomace and seeds	1376.0	-	412.0

Table 3: Proximate composition (g/100g dry sample), Water holding, oil holding capacity, total phenolic and scavenging activity of mango peel powder and mango kernel powder

Characteristics	Mango peel powder	Mango kernel powder
Moisture (%)	4.92± 0.32	6.57± 0.31
Ash (%)	3.88± 0.59	1.46± 0.06
Fat (%)	1.23± 0.10	8.15± 0.06
Protein (%)	3.6± 0.15	7.76± 0.30
Crude fibre (%)	9.33± 0.61	0.26± 0.07
Water holding capacity (g/g)	5.08 ±0.60	2.08± 0.12
Oil holding capacity (g/g)	2.02± 0.18	1.74± 0.10
Total phenolics (mg GAE/g)	19.06± 0.30	23.90± 0.33
Scavenging activity (%)	93.89± 0.20	95.08± 0.10

Source: Maisuthisakul & Gordon (2009)