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FRUITS WASTES: A RICH SOURCE OF BIOACTIVE CHEMICALS AND THEIR POTENTIAL APPLICATIONS

Dharmendra Singh*

*Institute of Pharmacy, Veer Bahadur Singh Purvanchal University, Jaunpur (U.P.) India

Abstract:

India is one of the world's leading fruit producing countries. After consumption, fruits leave behind waste that pollutes the environment as solid waste. In this article, we studied the surface, physical, and chemical properties of commonly available bulk fruit wastes (FW) such as bananas, oranges, citrus fruits, and lemons, and proposed their valuation in detail. Each fruit waste was subjected to a thorough final analysis of porosity, particle density, Fourier transform infrared characterized. Derivation of spectroscopy and TGA/thermogravimetry. The order of surface acidity is OW > LW > CW > BW. From the TG curve, it is clear that the FW is stable below 150 °C. The results will aid in the rational design of FW when used as bioactive compounds, phenolic antioxidants, organic acids, enzymes, biofertilizers, substrates for energy production, and adsorbents.

Introduction

India's agroclimate is very diverse and supports the cultivation of many crops, such as fruit trees, vegetables and ornamental plants. Root tubers and medicinal herbs as well as aromatic plants and spices and plantation crops are also cultivated. India is the second largest fruit and vegetable producer in the world. It is well known that a large amount of Lignocellulosic biomass is produced annually during the cultivation, harvesting and processing of agricultural products. Lignocellulose biomass can be used for a variety of purposes, such as a cheap biosorbent, as feedstock for the production of biochemicals and biofuels and as a substrate for the production of different enzymes and metabolites. Additionally, using these residues for the production of value-added products eliminates them from the environment as well as avoiding solid-waste processing.[1-2]

Bananas grow in hanging clusters, with three to twenty hands in each cluster and roughly twenty fruits per hands. A typical natural product weighs 125 g, consisting of approximately 25% dry matter and 75% water. About 30–40% (w/w) of new bananas make up banana waste (BW). The following make up the finished BW: ether extract (6.2%), solvent sugars (13.8%), rough protein (8%), and phenolic compounds (4.8%). BW primarily consists of low-molecular-weight substances such as pectin, cellulose, hemicellulose, and chlorophyll.[3–6] Bananas hold the position as the second most produced fruit globally, contributing to 16% of total fruit production worldwide. India leads in banana production, accounting for 27% of the global output. Oranges, classified under the Citrus sinesis species within the Rutaceae family, produce orange waste (OW) as a significant byproduct. OW comprises cellulose, hemicellulose, lignin, pectin (galacturonic acid), chlorophyll pigments, and various other low-molecular-weight compounds like limonene. Traditionally, OW undergoes processing to extract both volatile and nonvolatile fractions of essential oils and flavoring compounds. Additionally, OW has exhibited germicidal, antioxidant, and anticarcinogenic properties, indicating potential efficacy against breast and colon cancers, skin inflammation, muscle pain, stomach upset, and ringworm.[7–9]
Citrus, particularly Citrus limetta within the Rutaceae family, holds the distinction of being the world's largest produced fruit, accounting for 23% of global fruit production. Citrus waste (CW) emerges as a promising reservoir of specific essential oils, yielding approximately 0.5–3 kg of oil per tonne of fruit. These extracted essential oils find application across various sectors, including pharmaceuticals, confectioneries, cosmetics, alcoholic beverages, and in enhancing the shelf-life and safety of various food products. Additionally, CW is rich in pectin. The outer layer of lemon peel (Citrus limon, family Rutaceae), known as flavedo, displays a range of colors from green to yellow and serves as a valuable source of essential oils historically utilized in the flavoring and fragrance industries. Beneath the flavedo lies the albedo, the primary component of lemon peel,

characterized by its spongy, cellulosic nature and high dietary fiber content.[10-11] This research delves into the physical, chemical, and surface attributes of various fruit wastes, including banana, orange, citrus, and lemon. Utilizing a diverse array of analytical techniques such as gravimetric, titrimetric, potentiometric, and instrumental methods, alongside standard procedures for morphological and thermal analysis, the study aims to characterize these fruit wastes comprehensively. The findings yield valuable insights into the potential applications of fruit waste, thus enriching our knowledge of its versatile uses.

Materials and methods

Preparation Procedure:

Fruit residues, encompassing banana, orange, citrus, and lemon, were obtained from a local market in Jaunpur, Uttar Pradesh. These residues underwent meticulous cleaning to remove any leaves, sticks, or other unwanted materials. After thorough washing with tap water and double-distilled water to eradicate surface impurities, they were dried in an oven at 70 ± 2°C until achieving a uniform weight. The dried material was then ground and sieved, resulting in powdered fruit waste particles ranging in size from 0.106 to 0.90 mm, suitable for further characterization studies.

Physicochemical Characterization:

Proximate and ultimate analyses were performed on each type of fruit waste, assessing properties such as porosity, particle density, bulk density, point of zero charge, surface charges, water absorption capacity, and BET surface area. Furthermore, the samples underwent additional characterization using Fourier transform infrared spectroscopy (FTIR) and TG/DTG methods.

Results and discussion

The proximate and ultimate analysis results for FW are elaborated in Table 1, while the composition of FW is presented in Table 2. The relatively low moisture content (6%–10%) of FW enables extended storage periods with a reduced risk of mold formation, as moisture levels are limited or absent. This low moisture content promotes combustion, whereas high moisture hampers ignition and reduces the combustion temperature, adversely affecting the quality of combustion and the resulting reaction products.

The presence of ash content in FW indicates the presence of incombustible solid material. With ash content ranging from 5% to 6%, FW serves as a valuable source of various minerals and micronutrients for soil enrichment. The predominant volatiles (85%–87%) in FW are attributed to its organic nature. Organic components such as lipids, proteins, and carbohydrates in FW provide a rich source of nutrients.

The substantial volatile content of FW renders it easily ignitable and combustible, albeit with rapid combustion that can be difficult to control. Moreover, the significant volatile content impedes complete combustion. During combustion, devolatilization initiates at relatively low temperatures, releasing predominantly combustible gases like CO and H_2. Thus, the release and combustion of volatiles are vital factors to consider in the design and operation of combustion systems handling FW. However, the diverse compositions of FW may present challenges in designing such combustion systems.[12-14]

An optimal carbon-to-nitrogen ratio is crucial for promoting fungi growth. FW exhibits sufficient levels of carbon (38%–40%) and nitrogen (0.64%–1.3%), making it a suitable substrate for enzyme-production processes. Moreover, it contains a notable amount of oxygen (52%–54.55%), mainly due to the presence of carbohydrates and fiber. The significant presence of polymers, cellulose, and hemicellulose in FW suggests its potential as a bioadsorbent for synthetic organic pollutants.

The presence of carbon (38%–40%) and hydrogen (5.80%–6.20%) in these lignocellulosic biomass residues positions them as promising feedstocks for biogasification, which facilitates the production of syngas or hydrogen. Throughout the biomass gasification process of FW, alongside CO_2, H_2O, CO, CH_4, and H_2, other light (non-condensable) hydrocarbons (C_xH_y), condensable organic compounds (liquids at ambient conditions), and carbon-rich biochar are generated. Biochar, a byproduct, holds various potential uses, including gas production such as CO, and it serves as an adsorbent due to its porous nature.[15-17]

Table 1. Proximate and ultimate analysis of FW

	Proximate analysis					Ultimate analysis				
FW	Moisture (%)	Ash (%)	Volatile matter (%)	Fixed carbon (%)		N (%)	C (%)	H (%)	S (%)	O (%) (by difference)
BW	9.80	5.01	85.26	0.07		1.30	40.24	6.14	0.098	52.22
OW	7.91	5.25	86.70	0.14		1.15	38.91	6.19	0.11	53.64
CW	7.58	4.32	86.54	1.56		0.64	38.51	6.20	0.10	54.55
LW	6.10	5.40	87.16	1.34		1.27	40.33	5.96	0.19	52.25

Table 2. Composition of FW Value (% dry basis)

Parameters	BW	OW	CW	LW
Cellulose	12.17 ± 0.21	9.21	20.8	23.1
Hemicellulose	10.19 ± 0.12	10.50	17.2	8.09
Acid-detergent lignin	2.88 ± 0.05	0.84	8.9	7.6
Total sugars (sucrose + glucose + fructose)	29.83 ± 0.29	16.90	21.6	6.5
Pectin	15.9 ± 0.26	42.50	14.2	13.0
Ash	9.81 ± 0.42	3.50	3.0	2.5

Polyphenolics, fat and other extractives make up for the remainder of the composition.

Porosity, particle density, bulk density and waterabsorption capacity

Table 3 summarizes the determination of physical properties such as porosity, particle density, bulk density, and water-absorption capacity of FW. Among these properties, CW exhibits the lowest bulk density but the highest water-absorption capacity compared to other FWs. Conversely, OW displays the highest bulk density but the lowest percentage of porosity.

Differences in the bulk densities of FWs primarily arise from variations in particle size, particle shape, or both. As porosity increases, the volume of entrapped air also increases. The elevated water-absorption capacity of FW can be attributed to the high fiber content of peels, which contain numerous hydrophilic groups. Despite these advantageous characteristics, the low density of FWs complicates their processing, transportation, storage, and firing processes.[18]

Table 3. Physical properties of FW

	Bulk density (g/cc)	Particle density (g/cc)	Porosity (%)	Water absorption capacity (ml/g)
BW	0.39	0.89	56.41	5.1
OW	0.53	0.89	41.13	5.4
CW	0.38	1.06	63.91	6.7
LW	0.49	0.98	48.97	5.9

FTIR

FTIR spectra were utilized to identify the functional groups present on the surface of FW. Table 4 provides the FTIR peak values alongside the corresponding functional groups. The FTIR spectrum profiles of all FWs broadly confirm the presence of phenol, carboxylic acid, alcohol, alkanes, alkyl halide, amines, amino acids, and aromatics in each FW.

Specifically, the stretching absorption band centered at 3441.01 cm–1 corresponds to the OH or NH group in BW. The band observed at approximately 2891 cm–1 is attributed to the stretching vibrations of –CH3 or –CH2 groups in carboxylic acid, with its bending vibration observed at around 1367 cm–1. The peak at 1627 cm–1 is associated with the C=C stretch of alkene, aromatic, or amino acids. Additionally, the carbonyl stretching band of aldehyde is observed at 1735 cm–1, while peaks at 1232 cm–1, 1037 cm–1, and 715.59 cm–1 suggest the presence of phenol or tertiary alcohol, C–O stretch, and primary amine and CN stretch, respectively.

Table 4. FTIR peaks for FW

BW	OW	CW	LW	Analysis
3441.01	3352.82	3351.80	3342.98	Alcohols – H-bonded (–OH), Normal ‘polymeric’ OH stretch
2891.30	2919.84	2917.76	2918.94	Carboxylic acids (–OH)
1735.93	1739.86	1741.78	1736.91	C=O (aldehyde)

–	1691.92	1683.87	–	C=O (ketone–conjugated)
1627.92	1603.88	1604.83	1603.10	C=C (alkene, aromatic, amino acids)
–	1531.92	1533.87	–	Secondary amine group
1433.11	1460.89	1460.84	1451.11	Symmetric bending of CH3
1367.53	1398.99	1400.11	–	C–O (alcohols, ethers, esters)
1232.51	1265.82	1263.78	1243.95	Primary or secondary, OH in-plane bend, phenol or tertiary alcohol, OH bend
1037.70	1051.75	1054.66	1074.99	Primary alcohol, C–O stretch, primary amine, CN stretch
715.59	636.94	609.91	639.12	Alcohol, OH out-of-plane bend

In OW, the prominent bands observed at 3352, 2919, 1739, 1691, 1603, 1531, 1398, 1051.75, and 636.94 cm–1 are attributed to various stretching and bending vibrations. Specifically, these correspond to O–H stretching, C–O stretching, C=O stretching, N–H stretching, O–H stretching, C–O stretching, C=C stretching, and C–H stretching/bending vibrations, respectively. These bands indicate the presence of alcohol, phenol, carboxylic group, amines, amides, ketones, ester, ether, and amino acid groups in OW.

In CW, prominent peaks observed at 3351, 2917, 1741, 1683, 1604, 1533, 1400, 1054, and 609 cm–1 correspond to various stretching and bending vibrations. Specifically, these peaks are associated with O–H stretching, C–O stretching, C=O stretching, N–H stretching, O–H stretching, C–O stretching, C=C stretching, and C–H stretching/bending vibrations, respectively. These findings suggest the presence of alcohol, phenol, carboxylic group, amines, amides, ketones, ester, ether, and amino acids groups in CW.

In LW, strong bands are observed at 3342, 2918, 1736, 1603, 1074, and 639 cm–1, which correspond to various stretching and bending vibrations. Specifically, these bands indicate O–H stretching, C–O stretching, C=O stretching, N–H stretching, and O–H stretching/bending vibrations, respectively. These findings suggest the presence of alcohol, phenol, carboxylic group, amines, amides, and amino acids groups in LW.

Carboxylic acid found in FW possesses pharmaceutical properties and has been recognized for its therapeutic effects in treating various ailments such as ulcers, jaundice, headaches, stomatitis, hemicranias, fever, liver pain, and wounds in cattle. Additionally, it has been utilized in the treatment of edema and rheumatic joint pains. Furthermore, carboxylic acid renders FW suitable for metal adsorption applications. The primary sources of carboxylic acid in FW are typically pectin, cellulose, or lignin.[19-20] Amines, amides, and amino acids are the predominant groups present in FW, and their presence facilitates protein synthesis. The hydroxyl group in FW plays a crucial role in adsorbing anionic impurities, such as dyes. Notably, FW exhibits no peak between the regions of 2220 and 2260 cm–1, indicating the absence of cyanide groups. This confirms that the FWs studied do not contain any toxic substances.[21-22] The presence of amine, amide, and amino groups in FWs provides a valuable source of nitrogen.

Potential applications of FW

The valorization of FWs is closely linked to their composition and characterization, which can be broadly categorized into the following three groups: (a) Extraction of valuable compounds: This involves extracting bioactive chemicals, phenolic antioxidants, enzymes, carboxylic acid, and other valuable compounds from FWs. (b) Feedstock for energy generation: FWs can serve as feedstock for various forms of energy generation, including bioethanol, biomethane, biohydrogen, bio-oil, and gasification processes. (c) Other uses: FWs can also be utilized for other purposes such as biofertilizer production, as well as in the development of bioadsorbents and other applications.

Table 2 confirms that FW contains approximately 3% phenolic compounds. Some studies have explored the extraction of phenolic antioxidants from FW as reported in the literature. Moreover, FW can serve as a valuable feedstock for energy generation due to its composition, which includes lignin (0.8–9%), cellulose (9–59%), and hemicellulose (8–17%). Please refer to Table 2 for a comprehensive breakdown of the composition of FW.

With the high carbon (C) and hydrogen (H) content indicated in Table 3, along with a high LOI (Loss on Ignition) and the results obtained from TG/DTG analysis, it is evident that FW can be effectively utilized for gasification processes. Additionally, the values of bulk density and particle density of FW provided in Table 3 can aid in designing gasifiers with enhanced efficiency.

Recovery of chemicals

Table 2 indicates that phenolic and other extractive compounds make up approximately 15–20% by weight of

FW. The recovery of bioactive compounds from FW represents an efficient, cost-effective, and environmentally friendly method of utilizing these wastes while maximizing profits with minimal environmental impact. Extracts from BW predominantly contain polyphenols.[23] The total phenolic compounds found in these extracts range in composition from 0.90 to 3.0 g/100 g of dry BW. Additionally, BW extracts can yield 2,2-Diphenyl-1-picrylhydrazyl (DPPH) radical scavenging activity (8.45 ± 6.48%) and flavonoids (196.1 ± 6.70 mg/g). Other bioactive compounds, such as gallocatechin, pro-vitamin A compounds, trans-α-carotene, trans-β-carotene, β-cryptoxanthin, sterols, cycloartane-type triterpenes, polyunsaturated fatty acids, linolenic, and α-linolenic acids, can also be extracted from BW.[24-26] CW is known to contain essential oils that exhibit antimicrobial properties. Furthermore, CW serves as a rich source of natural flavonoids, including hesperidin, naringin, diosmin, and tangeretin. The production of essential oils from OW is economically viable and represents a high-value product. OW typically contains 5.436 kg of oil per 1000 kg of oranges, from which approximately 90% of D-limonene can be extracted.[27-30]

Phenolic antioxidant

FW contains significant quantities of phenolic antioxidants, as indicated in Table 2. BW, in particular, is abundant in gallocatechins, making it a valuable food source with potential benefits against heart disease and cancer. Components such as peel oil, phenols, lipids, and tannins found in BW have exhibited strong antimicrobial activity, suggesting their potential application in treating certain infections. Similarly, CW is rich in flavonoids and vitamin C, both of which possess antioxidant properties. These compounds have demonstrated effectiveness against clinical isolates of both Gram-positive and Gram-negative pathogenic bacteria, further highlighting their potential health benefits.[31-33]

Production of enzymes

The higher nitrogen and carbon content observed in FW, as shown in Table 1, confirms the presence of elevated levels of nitrogen and carbon in FW. This characteristic makes FW a promising substrate for enzymatic production. Enzymes such as α-amylase, cellulase, xylanase, laccase, manganese peroxidase, and lipase have been successfully obtained using BW as a substrate. CW has demonstrated superiority as a substrate for the production of pectinases, cellulases, and hemicellulases. LW has been reported to be utilized for the production of endopolygalacturonase.[34-36]

Energy production

Bio-ethanol production from FWs is viable due to the presence of cellulose, hemicellulose, and sugars, as indicated in Table 2. BW, in particular, has demonstrated potential as a substrate for ethanol production, with an optimal yield of 7.45% vol/vol achieved through coculturing Aspergillus niger and Saccharomyces cerevisiae for 7 days. In a pilot plant-scale study conducted by Zhou et al., ethanol production from CW resulted in 40 g/l ethanol, with limonene as a co-product, achieved through solid-state fermentation. Additionally, OW has been identified as a promising source of ethanol when subjected to enzymatic hydrolysis using different species of yeast and fungus.[37-42]

Bio-methane, which primarily consists of methane, can be generated anaerobically from various substrates using methanogenic bacteria. This conversion process is well-established and can be applied to FW for methane generation. Studies have reported methane yields ranging from 243 to 322 ml CH_4/g VS added from BW and 297 ml CH_4/g VS added from OW.[43-44]

Biofertilizer

FW is rich in micronutrients such as sodium (Na), potassium (K), calcium (Ca), zinc (Zn), and magnesium (Mg), all of which are essential for plant growth. Studies have demonstrated that these micronutrients contribute significantly to the agronomic value of FW. Research by Kalemelawa et al. evaluated both aerobic and anaerobic composting of inoculated BWs and assessed their agronomic value using various formulations, including BWs combined with cow dung, poultry litter, or earthworms. The resulting composts exhibited a high alkaline pH, suggesting their potential to reduce soil acidity. Vermicompost obtained from the decomposition of BW by earthworms, particularly Eudrilus eugeniae, has proven to be an effective biofertilizer. This vermicompost facilitates the uptake of nutrients by plants, thereby enhancing their growth and yield.[45-46]

As an adsorbent

The surface properties of FW suggest a prevalence of acidic sites and various functional groups, contributing to its rough and porous surface texture. This combination of characteristics renders FW well-suited for use as a bioadsorbent. FW has demonstrated effectiveness in the removal of heavy metals, dyes, and organic pollutants from aqueous solutions, with heavy metals exhibiting a particularly high affinity for FW.

FW serves as a cost-effective bioadsorbent, particularly BW and OW, which have been extensively studied and explored. Among various heavy metals and dyes, Pb2+ and methylene blue have been extensively investigated for their adsorption onto FWs. Studies have investigated BW for the removal of organic acids like benzoic acid, salicylic acid, and citric acid. Enhanced adsorption capacity has been observed in treated or modified FW compared to raw or untreated samples. Moreover, recent research has highlighted the efficiency of microwave-irradiated FWs as effective adsorbents.[47-48]

Conclusions

The physicochemical properties of FW have been thoroughly examined to gain deeper insights into each type of FW and explore their potential applications. We have discussed both the physical and chemical characteristics of FW, as well as their potential value-added applications and the limitations associated with their reuse. The higher hydrogen and carbon contents in FW contribute to increased heating value, while elevated levels of volatile substances make FWs well-suited for gasification. Additionally, the substantial presence of carbon and nitrogen renders FWs excellent substrates for enzymatic processes. Thermal analysis results have shown that a significant weight loss occurs within the temperature range of 150 to 400°C, primarily due to the decomposition of cellulose, hemicellulose, and lignin. FWs exhibit thermal stability below 150°C.

Furthermore, FW serves as a valuable source of bioactive compounds that can be converted into various value-added products. We have explored the utilization of FW as a substrate for producing bioactive compounds, phenolic antioxidants, organic acids, enzymes, biofertilizers, energy production, and as adsorbents.

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