

# Fruit peel waste: characterization and its potential uses

Pranav D. Pathak<sup>1</sup>, Sachin A. Mandavgane<sup>1,\*</sup> and Bhaskar D. Kulkarni<sup>2</sup>

<sup>1</sup>Department of Chemical Engineering, Visvesvaraya National Institute of Technology, Nagpur 440 010, India

<sup>2</sup>CSIR-National Chemical Laboratory, Pune 411 008, India

Globally, India is the leading producer of fruits. Fruits after consumption leave a peel which is a nuisance to the environment as a solid waste. In this article, commonly available large volume-fruit peels (FP) (viz. banana, orange, citrus, lemon and jackfruit) were investigated for surface, physical and chemical characteristics with a view to propose their valorization in detail. Each FP was characterized by proximate and ultimate analysis, porosity, particle density, bulk density, point of zero charge ( $\text{pH}_{\text{pzc}}$ ), surface pH, surface charges, water absorption capacity, BET surface area, scanning electron microscopy, Fourier transform infrared spectroscopy and TGA/derivative of thermogravimetric. The BET surface area of FP is very less, between 0.60 and 1.2  $\text{m}^2/\text{g}$ . The  $\text{pH}_{\text{pzc}}$  and surface pH values of orange peel (OP), citrus peel (CP), lemon peel (LP) and jackfruit peels (JFP) are in the range of 3–4. The  $\text{pH}_{\text{pzc}}$  value and surface pH of banana peel (BP) is closer to 7. The order of surface acidity is  $\text{OP} > \text{LP} > \text{CP} > \text{JFP} > \text{BP}$ . From TG curves it is clear that FPs are stable below 150°C. The results will be useful for rational design, when FP is used as a substrate for bioactive compounds, phenolic antioxidants, organic acids, enzymes, biofertilizer, production of energy and as adsorbents.

**Keywords:** Characterization, fruit peel, solid waste, utilization, valorization.

THE agro-climate of India is very diverse, encouraging the cultivation of numerous crops, including fruit trees, vegetables, ornamental plants, root tubers, medicinal herbs, aromatic plants, spices and plantation crops. India is the world's second largest producer of fruits and vegetables. It is well-known that huge quantities of lignocellulosic biomass are produced every year during cultivation, harvesting, processing and consumption of agricultural products. This biomass generated can be utilized for different applications such as (i) a low-cost biosorbent, (ii) feedstock for producing biochemical and biofuels, and (iii) a substrate for production of various enzymes and metabolites. Besides, using these residues to produce value-added products will eliminate them from the environment and avoid solid-waste handling<sup>1,2</sup>.

Banana (*Musa* sp., family Musaceae) develops in hanging clusters, with nearly 20 fruits/hand (tier) and 3–20 hands in each cluster. The average fruit weight is about 125 g with nearly 25% dry matter and 75% water. Banana peel (BP) comprises about 30–40% (w/w) of fresh banana. The composition of ripe BP is as follows: crude protein (8%), ether extract (6.2%), soluble sugars (13.8%) and total phenolic compounds (4.8%). The main components of BP are cellulose, hemicellulose, chlorophyll, pectin and other low-molecular weight compounds<sup>3–6</sup>. Banana is the second largest produced fruit, accounting for 16% of the total fruit production worldwide. India is the largest producer of banana, accounting for 27% of the world's total banana production.

Orange (*Citrus sinensis*, family Rutaceae) contains orange peel (OP) which is an important byproduct. OP comprises cellulose, hemicellulose, lignin, pectin (galacturonic acid), chlorophyll pigments and other low-molecular weight compounds (e.g. limonene). Traditionally, OP is treated to obtain volatile and nonvolatile fractions of essential oils and flavouring compounds. In addition, OP has been reported to have germicidal, antioxidant, and anticarcinogenic properties, and thus may be effective against breast and colon cancers, skin inflammation, muscle pain, stomach upset and ringworm<sup>7–9</sup>.

Citrus (*Citrus limetta*, family Rutaceae) is the world's largest produced fruit, accounting for 23% of the world's total fruit production. Citrus peel (CP) is a potential source of certain essential oils and yields about 0.5–3 kg oil/tonne of fruit. The essential oils extracted are used for various purposes, such as pharmaceuticals, confectioneries, cosmetics, alcoholic beverages, and also for improving the shelf-life and safety of various foodstuff. Besides, CP is also rich in pectin<sup>3,6,10</sup>.

Lemon (*Citrus limon*, family Rutaceae) peel's outer layer is called flavedo, the colour of which differs from green to yellow. Flavedo is a rich source of essential oils, that has been used since early times in flavouring and fragrance industries. The major component of lemon peel is albedo, which is a spongy and cellulosic layer under the flavedo and has high dietary fibre content<sup>11</sup>.

Jackfruit (*Artocarpus heterophyllus* L., family Mulberry) tree produces around 200–500 fruits annually. At maturity, each fruit weighs approximately 23–50 kg. About 59% of the fruit's outer peel is composed of fibre, which

\*For correspondence. (e-mail: sam@che.vnit.ac.in)

**Table 1.** Proximate and ultimate analysis of FP

FP	Proximate analysis				Ultimate analysis				
	Moisture (%)	Ash (%)	Volatile matter (%)	Fixed carbon (%)	N (%)	C (%)	H (%)	S (%)	O (%) (by difference)
BP	9.80	5.01	85.26	0.07	1.30	40.24	6.14	0.098	52.22
OP	7.91	5.25	86.70	0.14	1.15	38.91	6.19	0.11	53.64
CP	7.58	4.32	86.54	1.56	0.64	38.51	6.20	0.10	54.55
LP	6.10	5.40	87.16	1.34	1.27	40.33	5.96	0.19	52.25
JFP	6.48	6.32	86.28	0.92	0.90	40.04	5.86	0.12	53.08

**Table 2.** Composition of FP

Parameters	Value (% dry basis)				
	BP (ref. 73)	OP (ref. 61)	CP (ref. 48)	LP (ref. 48)	JFP
Cellulose	12.17 ± 0.21	9.21	20.8	23.1	nd
Hemicellulose	10.19 ± 0.12	10.50	17.2	8.09	nd
Acid-detergent lignin	2.88 ± 0.05	0.84	8.9	7.6	nd
Total sugars (sucrose + glucose + fructose)	29.83 ± 0.29	16.90	21.6	6.5	nd
Protein	5.13 ± 0.14	6.50	nd	7.0	nd
Pectin	15.9 ± 0.26	42.50	14.2	13.0	nd
Ash	9.81 ± 0.42	3.50	3.0	2.5	nd

Polyphenolics, fat and other extractives make up for the remainder of the composition. \*nd, not done.

is fairly rich in calcium and pectin. Jackfruit is a popular food ingredient in the tropical parts of the world<sup>12–14</sup>.

After consuming the edible part, the FPs are separated and dumped into municipal landfills. This causes serious pollution and disposal (solid-waste management) problems. Thus, utilization of FP for engineering applications serves dual purpose: (i) generating wealth from waste and (ii) as an efficient solid-waste abatement.

This study reports the physicochemical and surface characteristics of the following fruit peels: banana, orange, citrus, lemon and jackfruit. Gravimetric, titrimetric, potentiometric and instrumental methods were used to characterize them. Morphological and thermal analysis was carried out by applying standard methods. The results present an insight into various uses of FP and serves as baseline information to add to their growing list of potential applications.

## Materials and methods

### Sample preparation

The fruit peels of banana, orange, citrus, lemon and jackfruit were collected from a local fruit market in Nagpur, India. Their leaves, sticks and other unwanted fragments were then removed. After a thorough washing with tap water, peels were washed with double-distilled water to remove any physical impurity on the surface; it was then oven-dried at  $70 \pm 2^\circ\text{C}$  until a constant weight was

obtained. Finally, it was grounded and sieved. Powdered FP of particle size 0.106–0.90 mm was used for further characterization studies.

### Chemicals

All chemical reagents used in the analysis were of analytical grade, purchased from Fisher Scientific (USA) and used as obtained.

### Physicochemical characterization

Proximate and ultimate analyses of each peel were carried out and properties such as porosity, particle density, bulk density, point of zero charge, surface pH, surface charges, water absorption capacity, and BET surface area were determined. The samples were further characterized by scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR) and TG/DTG methods. A detailed outline of the characterization methods and instrumentation techniques used in this study were presented earlier<sup>15</sup>.

## Results and discussion

### Proximate and ultimate analyses

Results of proximate and ultimate analyses of FP are presented in Table 1. Table 2 shows the composition of

FP. Because of the low percentage of moisture (6%–10%), FPs can be stockpiled for a longer period, as threat of molds is significantly reduced in the absence of, or limited, moisture content. Low moisture helps in combustion, whereas high moisture hampers ignition and reduces the combustion temperature. This adversely affects the reaction products of combustion and quality of combustion<sup>16</sup>.

Ash represents an incombustible solid material. Ash (5–6%) is a good source of various minerals and micro-nutrients to soil. The higher amounts of volatiles (85–87%) are due to the organic nature of FP. Organic matters in FP are mainly lipids, proteins and carbohydrates, which can be a good source of nutrients<sup>17</sup>.

Because of high percentage of volatiles, FPs are easy to ignite and burn; however, the combustion is fast and difficult to control. In addition, the high volatile content prevents complete combustion. During combustion, devolatilization is initiated at a relatively low temperature and the released volatiles contain mainly combustible gases such as CO, H<sub>2</sub> and C<sub>x</sub>H<sub>y</sub>. Therefore, for design and operation of such combustion systems, the release and combustion of volatiles are important factors to be considered. However, at times, the varying compositions of FP may make it difficult to design such combustion systems<sup>16,18</sup>.

Good carbon-to-nitrogen ratio is necessary to cultivate fungi. FP contains sufficient amounts of carbon (38–40%) and nitrogen (0.64–1.3%), making them alternative and well-suited substrates for enzyme-production processes. It also has a good amount of oxygen (52–54.55%), attributed to the presence of carbohydrates and fibre. The high content of polymers, cellulose and hemicellulose in FP suggests that this could be a potential bioadsorbent for synthetic organic contaminants<sup>2</sup>.

The presence of carbon (38–40%) and hydrogen (5.80–6.20%) makes these lignocellulosic biomass wastes a potential feedstock for biogasification for production of syngas or hydrogen<sup>19,20</sup>. During biomass gasification of FP, along with CO<sub>2</sub>, H<sub>2</sub>O, CO, CH<sub>4</sub> and H<sub>2</sub>, other light (noncondensable) hydrocarbons (C<sub>x</sub>H<sub>y</sub>), condensable (liquids at ambient conditions) organic compounds, and carbon-rich biochar are also produced<sup>21</sup>. Biochar can be used for various purposes, including, production of gases such as CO. It can also be used as an adsorbent due to its porous nature<sup>12</sup>.

### Porosity, particle density, bulk density and water absorption capacity

Physical properties such as porosity, particle density, bulk density and water-absorption capacity of FP were determined (Table 3). As summarized in Table 3, CP has the lowest bulk density but the highest water-absorption capacity compared to other FPs. OP has the highest bulk density, but the lowest percentage of porosity.

The differences in bulk densities of the FPs are mainly due to differences in particle size, particle shape, or both<sup>22</sup>. The volume of entrapped air increases with increase in porosity. The high water-absorption capacity of FP is due to the high fibre content of peels, owing to a large number of hydrophilic groups. The low density of FPs, however, makes their processing, transportation, storage and firing complicated<sup>16</sup>.

### Point of zero charge and surface pH

A very useful parameter in adsorption studies is p*H*<sub>pzc</sub>. This gives an idea about ionization and the interactions between the adsorbent surface and the adsorbate. The p*H*<sub>pzc</sub> of FP was determined using the batch equilibration method. This method is based on the assumption that the protons, (H<sup>+</sup>) and hydroxyl groups (OH<sup>-</sup>) are possible determining ions. The H<sup>+</sup> or OH<sup>-</sup> from an aqueous medium are adsorbed onto the FP surface. The groups present on the surface of FP can either accept or donate an additional proton from the solution depending on solution pH and properties of FP. The surface becomes positively charged by accepting protons from the acidic solution; by contrast, it becomes negatively charged due to the loss of protons in a basic solution. The pH at which the surface of FP is neutral is known as p*H*<sub>pzc</sub><sup>23,24</sup>. The values of p*H*<sub>pzc</sub> were determined in double-distilled water (Figure 1 a) and in 0.01 N KNO<sub>3</sub> (Figure 1 b) solution. The results are presented in Table 4.

Adsorption of cations is favoured if pH > p*H*<sub>pzc</sub>, whereas the adsorption of anions is favoured if pH < p*H*<sub>pzc</sub>.

**Table 3.** Physical properties of FP

Peel	Bulk density (g/cc)	Particle density (g/cc)	Porosity (%)	Water absorption capacity (ml/g)
BP	0.39	0.89	56.41	5.1
OP	0.53	0.89	41.13	5.4
CP	0.38	1.06	63.91	6.7
LP	0.49	0.98	48.97	5.9
JFP	0.41	0.82	42.36	5.2

**Table 4.** Point of zero charge and surface pH of some FPs

FP	Point of zero charge		Surface pH	Reference
	DDW	0.1 N KNO <sub>3</sub>		
BP	5.36	4.98	6.68	This study
BP	–	2.41 (0.1 N KCl)	–	25
OP	4.1	3.88	3.61	This study
OP	3.9	–	–	25
CP	3.85	3.99	3.72	This study
LP	3.66	3.21	3.69	This study
JFP	4.86	4.16	4.87	This study

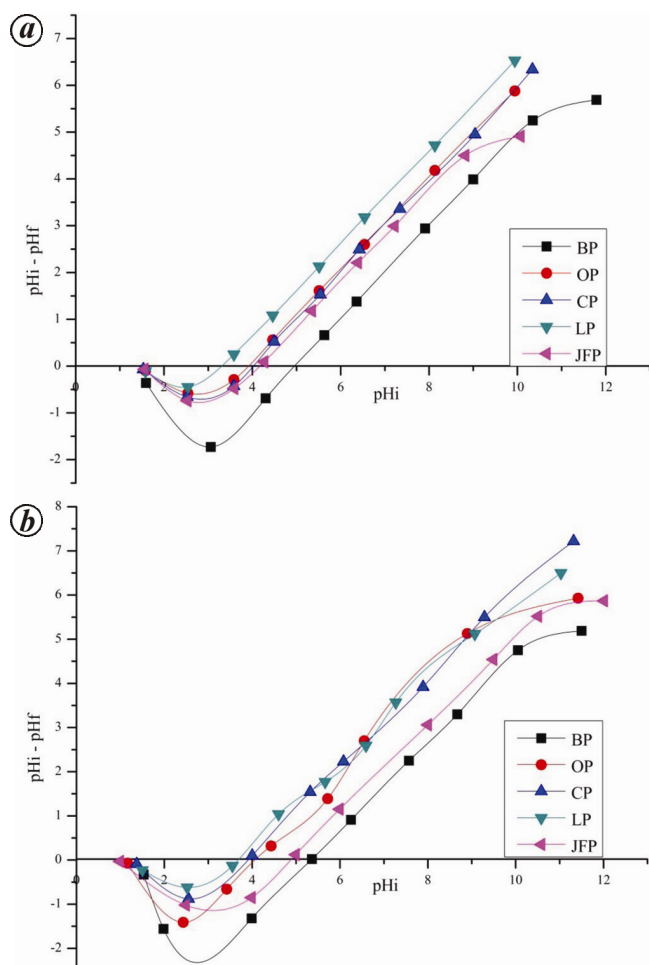
DDW, doubled distilled water.

The specific adsorption of cations shifts to lower values, whereas specific adsorption of anions shifts to higher values of  $\text{pH}_{\text{pzc}}$ .

The  $\text{pH}_{\text{pzc}}$  and surface pH values of OP, CP, LP and JFP are in the range of 3–4. This range suggests that the surface of these peels contains more acidic groups than basic groups. These peels are thus suitable for adsorption of cationic species. The  $\text{pH}_{\text{pzc}}$  value and surface pH of BP are closer to neutral pH, when compared to other peels. BP can thus be used for adsorption of both cationic and anionic moieties.

### Surface charges

The charges present on the FP surface determine whether the peel is acidic or basic in nature. The ratio of basic to acidic ( $B/A$ ) sites is presented in Table 5. If  $B/A < 1$ , then the surface has more positive charges; if  $B/A = 1$ , then the net charges present on their surface are equal; and if  $B/A > 1$ , then the surface has more negative charges.



**Figure 1.** Point of zero charge of FP in (a) distilled water and (b) 0.1 N  $\text{KNO}_3$  solution.

Among all the peels studied, the value of  $B/A$  was highest for BP (i.e. 6.53). This means that the available basic sites are six times more than the acidic sites. Literature also supports these values<sup>2</sup>.

Thus, it can be concluded that BP will be a better adsorbent of cationic species rather than anionic species. The order of surface acidity is as follows:  $\text{OP} > \text{LP} > \text{CP} > \text{JFP} > \text{BP}$ . The acidic surface favours adsorption of anions, whereas the basic surface favours adsorption of cations.

### BET surface area

The surface of FP is porous and rough in nature, as evident from the SEM images shown and discussed in the following section. The BET surface area of BP ( $0.65 \text{ m}^2/\text{g}$ ), OP ( $1.03 \text{ m}^2/\text{g}$ ), CP ( $1.14 \text{ m}^2/\text{g}$ ), LP ( $0.70 \text{ m}^2/\text{g}$ ) and JFP ( $1.15 \text{ m}^2/\text{g}$ ) is very low, when compared to siliceous materials. The BET surface area of BP is in the range of  $1.2\text{--}13 \text{ m}^2/\text{g}$ , whereas that of OP is in the range of  $2.14\text{--}47.03$  (ref. 25).

The low surface area is possibly due to the operational complexity of degassing lignocellulosic samples<sup>26</sup>. Moreover, the low surface area is a characteristic feature of carbonaceous materials<sup>27</sup>.

### FTIR

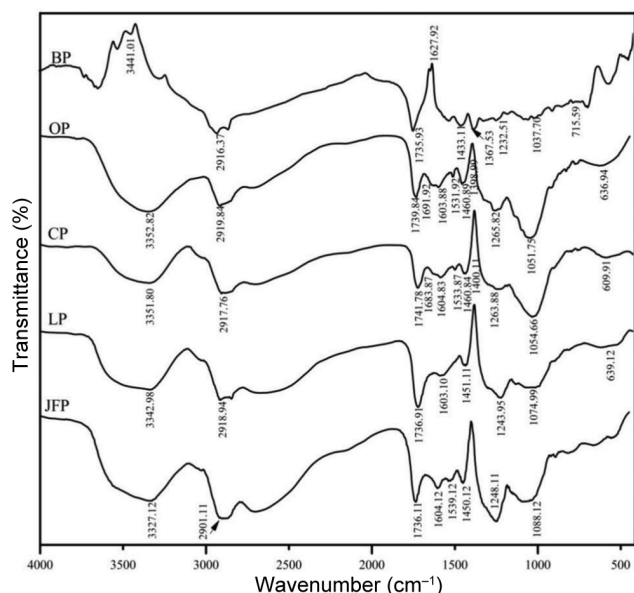
FTIR spectra were obtained to recognize the functional groups present on the FP surface. Table 6 presents the FTIR peak values and the corresponding functional groups. FTIR spectrum profiles of all FPs (Figure 2) broadly confirm the presence of phenol, carboxylic acid, alcohol, alkanes, alkyl halide, amines, amino acids, aromatic in each FP. The stretching absorption band centred at  $3441.01 \text{ cm}^{-1}$  represents the OH or NH group in BP. The band observed at around  $2891 \text{ cm}^{-1}$  is assigned to stretching vibrations of  $-\text{CH}_3$  or  $-\text{CH}_2$  groups in carboxylic acid and its bending vibration is observed at around  $1367 \text{ cm}^{-1}$ . The peak at  $1627 \text{ cm}^{-1}$  is assigned to the C=C stretch of alkene, aromatic or amino acids. The carbonyl stretching band of aldehyde is observed at  $1735 \text{ cm}^{-1}$ . The peaks at  $1232 \text{ cm}^{-1}$ ,  $1037 \text{ cm}^{-1}$  and  $715.59 \text{ cm}^{-1}$

**Table 5.** Surface charges on FP

FP	Available sites ( $\text{mmol g}^{-1}$ )			Basic sites/acidic sites (B/A)
	Acidic	Basic	Total	
BP	0.75	4.90	5.65	6.53
OP	4.05	0.75	4.80	0.19
CP	3.65	1.25	4.90	0.34
LP	3.95	1.00	4.95	0.25
JFP	2.85	1.25	4.10	0.44

**Table 6.** FTIR peaks for FP

Obtained peaks					Analysis
BP	OP	CP	LP	JFP	
3441.01	3352.82	3351.80	3342.98	3327.12	Alcohols – H-bonded (–OH), Normal ‘polymeric’ OH stretch
2891.30	2919.84	2917.76	2918.94	2901.11	Carboxylic acids (–OH)
1735.93	1739.86	1741.78	1736.91	1736.11	C=O (aldehyde)
–	1691.92	1683.87	–	–	C=O (ketone–conjugated)
1627.92	1603.88	1604.83	1603.10	1604.12	C=C (alkene, aromatic, amino acids)
–	1531.92	1533.87	–	1539.12	Secondary amine group
1433.11	1460.89	1460.84	1451.11	1450.12	Symmetric bending of CH <sub>3</sub>
1367.53	1398.99	1400.11	–	–	C–O (alcohols, ethers, esters)
1232.51	1265.82	1263.78	1243.95	1248.11	Primary or secondary, OH in-plane bend, phenol or tertiary alcohol, OH bend
1037.70	1051.75	1054.66	1074.99	1088.12	Primary alcohol, C–O stretch, primary amine, CN stretch
715.59	636.94	609.91	639.12	–	Alcohol, OH out-of-plane bend

**Figure 2.** FTIR of FP.

suggest the presence of phenol or tertiary alcohol, C–O stretch, and primary amine and CN stretch respectively.

In OP, the intense bands seen at 3352, 2919, 1739, 1691, 1603, 1531, 1398, 1051.75 and 636.94  $\text{cm}^{-1}$  correspond to the O–H/C–O stretching/C=O/N–H/O–H stretching/C–O/C=C/C–H stretching/bending vibrations respectively, and indicate the presence of alcohol, phenol, carboxylic group, amines, amides, ketones, ester, ether and amino acid group in OP.

CP shows strong peaks at 3351, 2917, 1741, 1683, 1604, 1533, 1400, 1054 and 609  $\text{cm}^{-1}$  correspond to the O–H/C–O stretching/C=O/N–H/O–H stretching/C–O/C=C/C–H stretching/bending vibrations respectively, indicating the presence of alcohol, phenol, carboxylic group, amines, amides, ketones, ester, ether and amino acids groups.

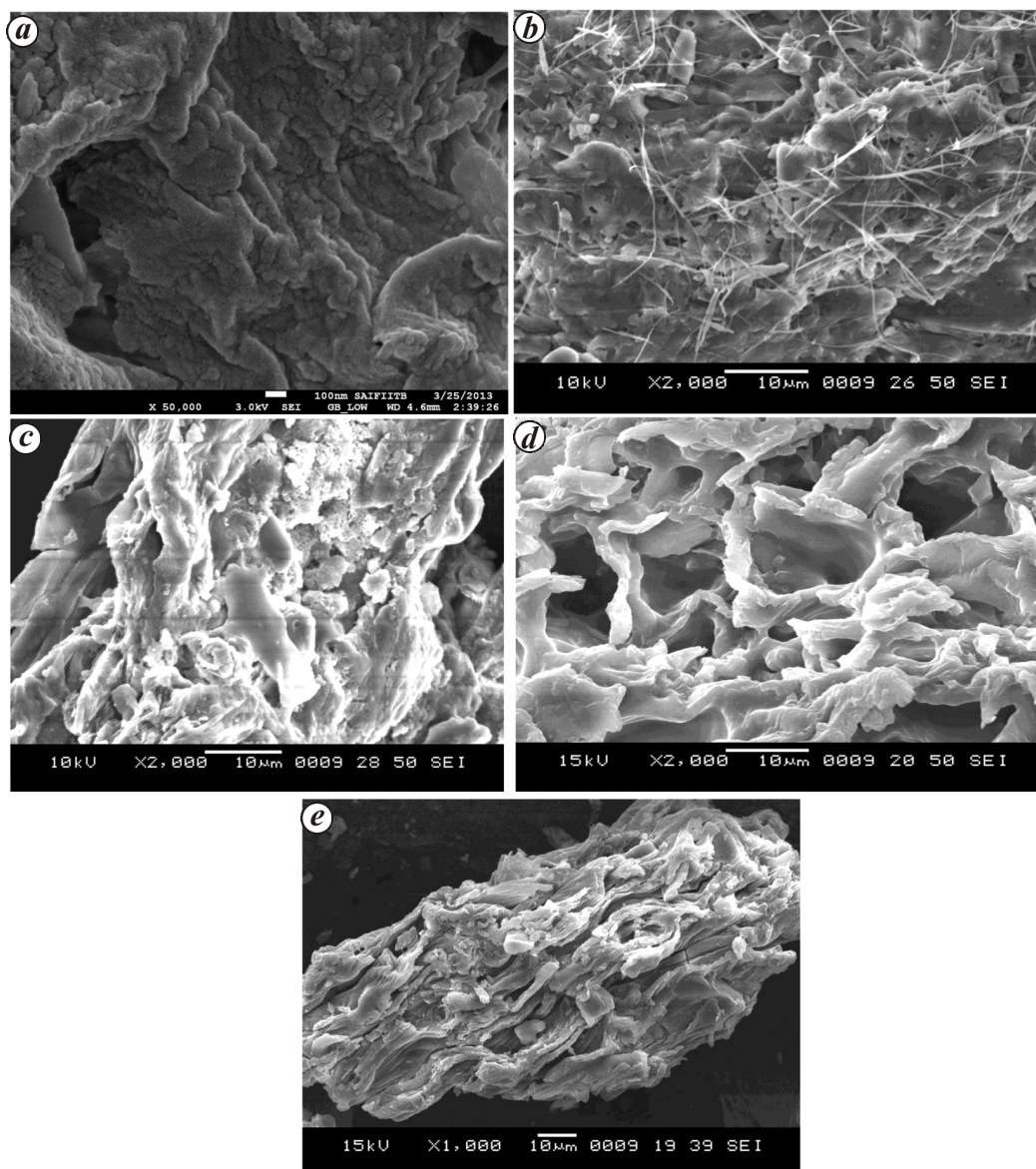
LP shows robust bands occurring at 3342, 2918, 1736, 1603, 1074 and 639  $\text{cm}^{-1}$ , which correspond to the O–H/C–O stretching/C=O/N–H/O–H stretching/bending vibrations respectively, indicating the presence of alcohol, phenol, carboxylic group, amines, amides and amino acids group.

JFP shows strong peaks at 3327, 2901, 1736, 1604, 1539 and 1088  $\text{cm}^{-1}$ , which correspond to the O–H/C–O stretching/C=O/N–H/O–H stretching/C=C/C–H stretching/bending vibrations respectively, indicating the presence of alcohol, phenol, carboxylic group, amines, amides, ketones and amino acids group.

Carboxylic acid present in FP has pharmaceutical properties. It is helpful in curing diseases such as ulcers, jaundice, headache, stomatitis, hemicranias, fever, pain in liver, and wounds in cattle as well as in the treatment of edema and rheumatic joint pains<sup>28</sup>. Besides, carboxylic acid also makes FP suitable for metal adsorption. The major source of carboxylic acid in FP is either pectin or cellulose or lignin<sup>29,30</sup>. Amines, amides, and amino acids are the main groups in FP, and owing to their presence FP can be used for protein synthesis. The hydroxyl group in FP plays a vital role in adsorption of anionic impurities such as dyes. FP does not show any peak between the regions 2220 and 2260  $\text{cm}^{-1}$ , which suggests the absence of cyanide groups, confirming that FPs studied do not contain any toxic substances<sup>28,31</sup>. The amine, amide and amino groups in FPs are a good source of nitrogen.

### SEM

A microscopic observation displays particle geometry and structural variations of the surface. The surface of FP is uneven, rough and contains some fibres; additionally, the particle shape and sizes are also different. The particles vary in shape from spherical to long flakes. In addition, some macropores and micropores are observed on the surface.



**Figure 3.** Scanning electron micrographs of (a) BP; (b) OP; (c) CP; (d) LP; (e) JFP.

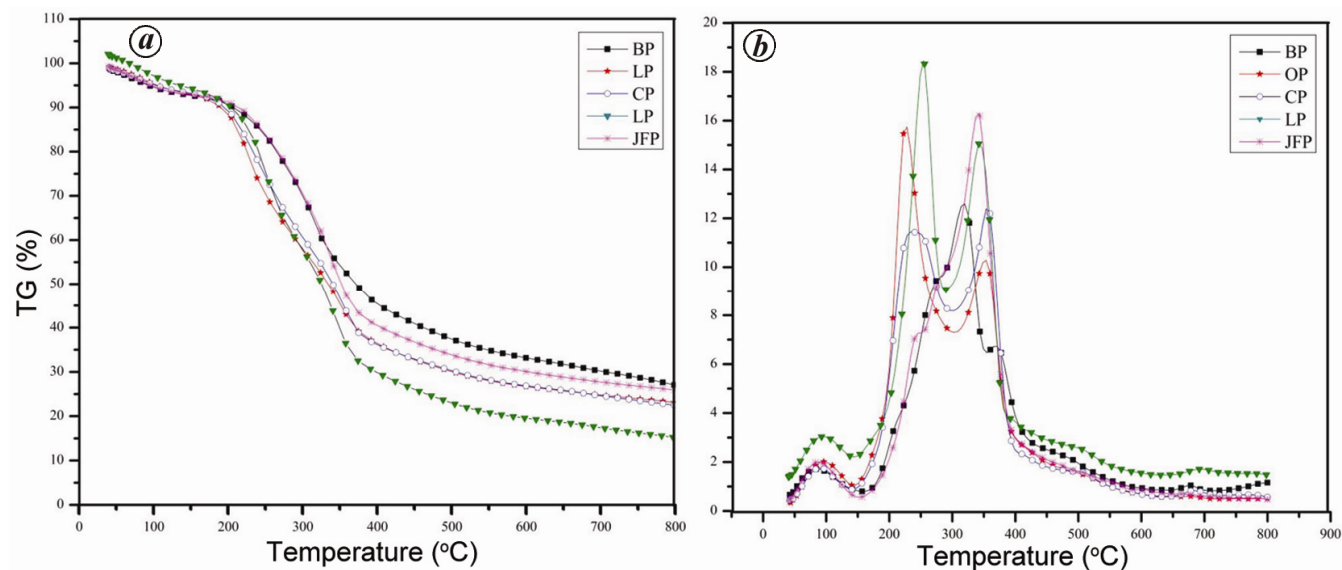
The surface of BP is rough and porous (Figure 3 *a*). Though the surface of OP (Figure 3 *b*) is also rough, it additionally contains some fibres that are spread throughout the surface. Compared to BP, the number of pores on the OP surface is less. CP (Figure 3 *c*) shows an irregular surface with negligible and tiny pores. The LP surface (Figure 3 *d*) is typically asymmetrical and highly porous. In addition, its surface (LP) contains a larger number of pores when compared to other FPs. JFP has long flakes like structure (Figure 3 *e*) containing a rough surface with tiny pores.

### TGA

The thermal analysis of FPs was performed to understand their thermal stability. The thermogravimetric (TG) and

derivative of thermogravimetric (DTG) curves of each FP undergoing pyrolysis under an atmosphere of nitrogen at a heating rate of  $30^{\circ}\text{C min}^{-1}$  are shown in Figure 4 *a* and *b* respectively. In the TG curve, the first weight loss was observed between  $150^{\circ}\text{C}$  and  $200^{\circ}\text{C}$ . This loss in weight can be attributed to removal of moisture and volatile organic materials such as oils, terpenes and pigments. The second weight loss is observed between  $150^{\circ}\text{C}$  and  $400^{\circ}\text{C}$ . This weight loss corresponds to decomposition of cellulose and hemicellulose. There is no significant weight loss observed after  $700^{\circ}\text{C}$ . This is due to the presence of fixed carbon, which is stable at higher temperature.

The DTG curves of FP show two decomposition peaks at temperatures between  $200^{\circ}\text{C}$  and  $250^{\circ}\text{C}$  and  $300^{\circ}\text{C}$  and  $400^{\circ}\text{C}$ . Both BP and JFP show weak decomposition peaks at  $200^{\circ}\text{C}$ – $250^{\circ}\text{C}$ , whereas OP, CP and LP show a sharp



**Figure 4.** *a*, Thermogravimetric analysis of different FPs. *b*, Differential thermogravimetric analysis (DTG) of different FPs.

peak. The first decomposition peak between 200°C and 250°C corresponds to pectin and hemicellulose in FP. The second decomposition peaks between 300°C and 400°C represent cellulose decomposition. The tailing section of all DTG curves appears to be flat. This flat tailing section of the DTG curves at higher temperature represents the presence of lignin, which is known to decompose gradually over wide range of temperatures.

The decomposition of bituminous coal starts at about 350°C, which is much higher than the one corresponding to FP (200°–250°C). This indicates that FP is more combustible at lower temperatures. Therefore, FP has a higher potential for energy production by pyrolysis and gasification<sup>31–35</sup>.

From the TG curves obtained, it is clear that FPs are stable below 150°C. Thus, below this temperature, FP can be utilized as an adsorbent in its natural or modified form.

### Potential applications of FP

Valorization of FPs is related to their composition and characterization and can be broadly classified under the following three categories: (a) extraction of valuable compounds (bioactive chemicals, phenolic antioxidants, enzymes, carboxylic acid, etc.); (b) feedstock for energy generation (bioethanol, biomethane, biohydrogen, bio-oil, gasification, etc.); (c) other uses (biofertilizer, bioadsorbents, etc.)

Table 2 confirms that FP contains (3%) phenolic compounds<sup>36</sup>. Certain studies have also reported on the extraction of phenolic antioxidants from FP<sup>37</sup>. In addition, FP can be used as feedstock for energy generation as it contains lignin (0.8–9%), cellulose (9–59%) and hemicellulose (8–17%); see Table 2 for complete composition.

Based on the high C and H content (Table 3), high LOI<sup>38</sup>, and the results of TG/DTG study (Figure 4), it can be ascertained that FP can be effectively used for gasification. The values of bulk density and particle density of FP (Table 3) help to design the gasifier with better efficiency.

Surface properties such as surface pH, point of zero charge (Table 4), surface acidity-to-basicity ratio (Table 5) and FTIR (Table 6 and Figure 2) make them efficient low-cost bioadsorbents.

### Recovery of chemicals

Table 2 shows that phenolic and other extractive compounds constitute up to 15–20% wt/wt of FP. Recovery of bioactive compounds from FP is an effective, economical, and green way of utilizing these wastes with minimum impact to the environment, yet with higher profits. BP extracts mainly contain ‘polyphenols’<sup>39</sup>. The total phenolic compounds present in these extracts vary in composition from 0.90 to 3.0 g/100 g of dry BP<sup>36</sup>. 2,2-Diphenyl-1-picrylhydrazyl (DPPH) radical scavenging activity ( $8.45 \pm 6.48\%$ ) and flavonoids ( $196.1 \pm 6.70$  mg/g) can also be extracted from BP<sup>40</sup>. Some other bioactive compounds such as gallic acid, pro-vitamin A compounds, trans- $\alpha$ -carotene, trans- $\beta$ -carotene,  $\beta$ -cryptoxanthin, sterols cycloartane-type triterpenes, polyunsaturated fatty acids, linolenic, and  $\alpha$ -linolenic acids can also be extracted from BP<sup>40–42</sup>. CP contains essential oils that are recognized antimicrobial agents. CP is a rich source of natural flavonoids (hesperidin, naringin, diosmin and tangeretin)<sup>43</sup>. Essential oil production from OP is economically possible, and is a high-value product. OP contains 5.436 kg of oil per 1000 kg of oranges, from

which approximately 90% of D-limonene can be extracted<sup>44-46</sup>.

### Phenolic antioxidant

Large amounts of phenolic antioxidants are present in FP (Table 2). BP is rich in gallo catechins, which makes it a useful food source against heart disease and cancer<sup>37</sup>. Peel oil, phenols, lipids and tannins present in BP have demonstrated good antimicrobial activity, and thus, can be used for treating certain infections<sup>47</sup>. CP is rich in flavonoids and vitamin C, which possess antioxidant properties<sup>43,48</sup>. JFP contains antimicrobial compounds, such as furanone, furfural and benzenetriol, all of which are beneficial against clinical isolates of Gram-positive and Gram-negative pathogenic bacteria<sup>49</sup>.

### Organic acid

Organic acid production from FP is advantageous due to its low cost. Citric acid was produced from BP by Koji fermentation using *Aspergillus niger* MTCC 282 (ref. 50). For production of succinic acid from OP, CP and LP, various bacteria (*Actinobacillus succinogenes*, *Anaerobiospirillum succiniciproducens*, *Mannheimia succiniciproducens*), yeast (*S. cerevisiae*) and fungi (*Byssoschlamys nivea*, *Aspergillus*, etc.) were used. Similarly, citric acid was produced using OP<sup>48</sup> and JFP<sup>51</sup>. Lactic acid was produced by the action of *Rhizopusoryzae* NCIM 1009 using CP as substrate<sup>52</sup>.

### Production of enzymes

Higher nitrogen content and carbon ultimate analysis (Table 1) confirm the presence of higher nitrogen and carbon in FP. This makes FP a potential substrate for enzymatic production<sup>2</sup>. Enzymes such as  $\alpha$ -amylase<sup>53</sup>, cellulase<sup>54</sup>, xylanase, laccase, manganese peroxidase<sup>55</sup> and lipase<sup>56</sup> were obtained using BP as substrate. CP proved to be a better substrate for production of pectinases, cellulases and hemicellulases<sup>48</sup>. LP is reported to be used for production of endopolygalacturonase<sup>48</sup>. Cellulase<sup>57</sup> and  $\beta$ -D-fructofuranosidase<sup>58</sup> can also be produced using JFP as substrate.

### Energy production

**Bio-ethanol:** Because of the presence of cellulose, hemicellulose and sugars (Table 2), FPs are a good substrate for production of ethanol. The optimal yield of ethanol from BP was 7.45% vol/vol, which involved co-culturing *Aspergillus niger* and *Saccharomyces cerevisiae* for 7 days using BP as substrate<sup>59</sup>. Zhou *et al.*<sup>60</sup> in a pilot

plant scale obtained 40 g/l ethanol with limonene as co-product from CP by solid-state fermentation<sup>60</sup>. OP is also a good source of ethanol, when it is subjected to enzymatic hydrolysis using different species of yeast and fungus<sup>61</sup>. Using JFP as a substrate, 4.64 g/l of ethanol was obtained by fermenting *S. cerevisiae* for 96 h (ref. 62).

**Bio-methane:** Methane, the main constituent of natural gas, can be produced from a variety of substrates anaerobically using methanogenic bacteria. The conversion process is well-defined and can be utilized for generation of methane from FP. Methane yields of 243–322 and 297 (ml CH<sub>4</sub>/g VS<sub>added</sub>) were obtained from BP and OP respectively<sup>63</sup>. JFP can be used for the production of methane with the successive addition of mango, tomato, orange peels with oil, deoiled orange, banana and pineapple waste<sup>64</sup>.

**Bio-hydrogen:** Hydrogen is a renewable, clean and promising future fuel. Hydrogen production by biological route using waste biomass is a recent research area. Bio-hydrogen production from food and food-processing waste containing large amounts of cellulose (e.g. JFP) provides higher bio-hydrogen yields<sup>65</sup>. Other peels can also be used for bio-hydrogen production.

**Gasification:** From proximate and ultimate analyses (Table 1), it is clear that FP has high H, C and volatile content, lower ash and moisture content; additionally, from TG/DTG analysis, it is observed that FP can be decomposed at lower temperatures. These thermogravimetric properties make FP a potential choice for gasification for generation of energy by producing gases such as H<sub>2</sub>, CO and CH<sub>4</sub>. The byproducts of gasification (i.e. bio-char and bio-oil), also have their multiple applications. Biomass does not add additional CO<sub>2</sub> to the environment as it utilizes identical amount of C in growing during its life and is released in the environment when used as fuel<sup>66</sup>. Soetardji *et al.*<sup>67</sup> pyrolysed JFP and obtained 51.8% yield of bio-oil at 550°C (ref. 67).

### Biofertilizer

FP contains substantial amounts of micronutrients such as Na, K, Ca, Zn and Mg which are essential for plant growth<sup>17,48,68</sup>. Kalemelawa *et al.*<sup>69</sup> evaluated aerobic and anaerobic composting of inoculated BPs and assessed their agronomic value using a formulation containing BPs and either cow dung, poultry litter or earthworms. The high alkaline pH of BP compost suggests that it may potentially reduce soil acidity. Vermicompost obtained by decomposition of BP by earthworm (*Eudrilus eugeniae*) is an effective biofertilizer that facilitates uptake of nutrients, thereby improving the yield and growth of plants<sup>70</sup>.



*As an adsorbent*

The surface properties of FP indicate that it has more acidic sites and different functional groups with rough and porous surface. This blend of properties makes it suitable as a bioadsorbent. Heavy metals, dyes and organic pollutants can be successfully removed from aqueous solution using FP, as heavy metals show higher affinity toward FP.

Pathak *et al.*<sup>25</sup> provided a critical review on use of FP as a low-cost bioadsorbent. They concluded that BP and OP are extensively studied and explored FPs. Of the different heavy metals and dyes, Pb<sup>2+</sup> and methylene blue are extensively studied for their adsorption on FPs. Pathak *et al.*<sup>71,72</sup> explored BP for removal of organic acids such as benzoic acid, salicylic acid and citric acid. Surface pH of BP is 6.68 (Table 4) and the ratio of basic sites to acidic sites is 6.53 (Table 5), which makes them suitable for adsorption of cations. Treated/modified FPW shows better adsorption capacity, compared with raw or untreated samples. A recent study reported that microwave-irradiated FPs are efficient adsorbents<sup>72</sup>.

**Conclusions**

The physicochemical properties of FP have been determined to obtain further insight into each FP and study their potential applications. In particular, we have discussed the physical and chemical characteristics of FP, their potential value-added applications and the limitations of FP reuse.

The higher hydrogen and carbon contents increase the heating value of FP; besides, higher amounts of volatile substances in FPs make them ideal for gasification. Carbon and nitrogen are present in high amounts in FP, making them good substrates for enzymatic process. The point of zero charge and surface pH for OP, CP, LP, and JFP are acidic, whereas those of BP are close to neutral. Surface charges indicate that OP, CP, LP, and JFP have larger number of acidic sites and hence can be used as an adsorbent of cationic moieties. The FP surface as seen on an SEM image is rough, irregular, and fibrous and contains some macropores and micropores. Of all FPs studied, LP has more pores and OP has a fibrous surface. Results of thermal analysis indicate that a majority of weight loss occurs in the range of 150°–400°C, which is mainly due to decomposition of cellulose, hemicellulose and lignin. FPs are, however, thermally stable below 150°C. FP is also a valuable source of bioactive compounds, which can be converted into value-added products. We have discussed the utilization of FP as a substrate to bioactive compounds, phenolic antioxidants, organic acids, enzymes, biofertilizer, energy production and adsorbents.

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