Characterizing fruit and vegetable peels as bioadsorbents

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Fruit and vegetable peel (FVP) wastes are a commonly generated organic waste from both households and food-processing industries. However, FVPs are low-cost lignocellulosic materials that have some potential for reutilization. For its particular reutilization, the characterization of FVP is essential. In this regard, the present study provides a detailed physico-chemical characterization of commonly used FVPs such as pomegranate, pineapple, watermelon, garlic, green pea and pigeon pea. The materials were characterized by SEM, FTIR and TGA/DTG. Various properties of these materials, such as porosity, particle density, bulk density, surface charges, point of zero charge, surface pH, water absorption capacity and BET surface area were determined. The BET surface area of FVP was found in the range 1.0–1.4 m^2/g. Water absorption capacity was highest for watermelon peel (11.5 ml/g), while it was lowest for pigeon pea peel (5.5 ml/g). Point of zero charge and surface pH of all FVPs were in the acidic range 3–6. The surface of FVP was irregular and rough with some pores. Thermal analysis showed that FVPs are thermally stable below 150°C. The results of this study provide an understanding of the properties of FVPs and suggest that the materials can be used as a low-cost adsorbent.

Keywords: Bioadsorbent, fruit and vegetable peels, organic waste, physico-chemical characterization.

FRUIT and vegetable peel (FVP) wastes are commonly generated from both households and food-processing industries. Although the amount of these organic wastes generated from households is negligible, that generated from food-processing industries is large, as they are a major by-product in these industries. The FVP wastes often causes serious problems in municipal landfills due to their high biodegradability[1]. However, these wastes can be potentially used as a low-cost biosorbent. In addition, using these wastes in various other potential applications will eliminate them from the environment and reduce solid-waste handling, which will add some value to these wastes[2,3].

Pomegranate (*Punica granatum* L., family Punicaceae) is a small tree growing up to 5–8 m in height and mostly cultivated in the Iranian Plateau, the Himalayas in northern India, North Pakistan, Azerbaijan, Afghanistan, the Mediterranean region and Russia. Over centuries, different parts of the tree such as leaves, flowers, barks, fruits and seeds have been used to cure diseases. Because of its high nutritional value, pleasant taste and many medicinal properties, it is one of the most popular fruits in the world. Pomegranate fruits are normally eaten fresh or as a processed product (e.g. wine, juice, jam and sauce for salad). Pomegranate peel (PP) is a by-product from the juice industry and therefore is inexpensive. It constitutes 5–15% of the total weight of the fruit[4–6].

Pineapple (*Ananas comosus* Merr., family Bromeliaceae) is a herbaceous, perennial plant native to the southern parts of Brazil and Paraguay. The tree grows to a height of 1.0–1.5 m. The fruit is predominantly eaten fresh and mainly added in fruit cocktail, salad, dessert, juice and jam. This is another fruit that is commonly used in the food-processing industries. The fruits are harvested throughout the year and only 52% of the total fruit is utilized for different industrial processes. The remaining 48% includes the peel and leaves containing high cellulose and lignin, which are difficult to degrade. Pineapple peel (PAP) constitutes approximately 35% of this remaining portion[7–9].

Watermelon (*Citrullus lanatus*, family Cucurbitaceae) is an annual plant with long, weak, trailing, or climbing stems, which are five-angled and up to 3 m long. The plant is originally from Egypt, but is now grown in India and China as well. In this fruit, only the inner red fleshy portion is sweet and edible, and is used for making juice and salad or eaten afresh. The remaining portion, which consists of about 35% rind and 15% peel (WMP), is considered as waste, and has no commercial value[10,11].

Garlic (*Allium sativum*, family Amaryllidaceae) is native to Central Asia and has long been cultivated in the Mediterranean region. It is also cultivated in Africa, Asia and Europe during certain suitable seasons. Garlic is a bulbous plant that grows up to 1.2 m in height. Generally, garlic is used as a food ingredient and also in some pharmaceutical applications. Because of its wide applications, garlic peel (GP) is easily obtained as waste in large volumes[12,13].

Green pea (*Pisum sativum*, family Fabaceae) plant grows thin tendrils (modified leaves) that coil around any accessible support and can climb up to 1–2 m in height.

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After removing the peas from their pods, 35–40% of solid waste (green pea peels; GPPs) is generated.

Pigeon pea (*Cajanus cajan*, family Fabaceae) primarily originated in the eastern part of peninsular India. The seeds of this plant have become a common food grain in many parts of the world including Africa, Asia and Latin America. Pigeon pea is a small tree and grows about 1–2 m in height. The dry matter yield of pigeon pea peel (PIP) is almost equal to that of its seed[14].

We studied the surface and physico-chemical characteristics of PP, PAP, WMP, GP, GPP and PIP. The materials were characterized by titrimetric, potentiometric, gravimetric and instrumental analysis. Standard methods were used for morphological and thermal analysis. The results of this study provide an understanding of the properties of FVPs and suggest that the material can be used as a low-cost adsorbent.

Materials and methods

Preparation of samples

FVPs of PP, PAP, WMP, GP, GPP and PIP were obtained from a local market in Nagpur, Maharashtra, India. The peels were washed with double-distilled water (DDW) and dried at 70 ± 2°C in a hot-air oven until constant weight was obtained. The dried product was then ground and sieved. Powdered FVPs of particle size measuring 0.106–0.90 mm were used for the characterization studies.

Chemicals

All chemical reagents used in the titration were supplied by Fisher Scientific, USA and were of analytical grade.

Instrumentation and characterization of FVP

Proximate and ultimate analyses of FVP were carried out to determine the ash percentage and contents of moisture, fixed carbon and volatile matter. Properties of FVP particles such as porosity, particle density, bulk density, surface charges, point of zero charge, surface pH, water absorption capacity and BET surface area were determined. FVPs were further characterized by Fourier transform infrared spectra (FTIR), scanning electron microscope (SEM) and thermogravimetric weight loss (TG) and derivative of thermogravimetric (DTG) studies.

The compositions of carbon, hydrogen and nitrogen were determined with an Elemental Analyzer (vario MACRO cube, Elementar, Hanau, Germany). A pH meter (Evtech Instrument, model pH 2700) with a glass electrode was used for measuring pH of the aqueous solution. The BET surface area of FVP was determined using a surface area analyser (Smart Sorb 92/93). FTIR spectra of FVP were recorded using KBr disk (Perkin–Elmer, Spectrum-1). Scanning electron microscopy (JSM-6380A) was used to examine the morphology of the powders. Thermogravimetric analysis using Hitachi TG/DTA 7200 was carried out to obtain the weight loss. Differential scanning calorimetry (DSC) was performed to obtain phase change as a function of temperature. The samples were heated in air at the rate of 30°C/min up to 800°C in N_2 atmosphere.

Proximate analysis

Proximate analysis of FVP was done according to standard procedure[15]. Moisture content of FVP was calculated as given in eq. (1). FVP sample was kept in a hot-air oven at 102 ± 2°C till constant weight was obtained. Then the sample was kept in a desiccator till it reached room temperature and finally the weight of the sample was taken to determine the loss in weight due to the removal of moisture. Volatile matter was determined by heating the air-dried sample of FVP in muffle furnace at 900 ± 10°C for 7 min and calculated using eq. (2). To determine percentage ash content, the air-dried FVP sample was heated in a muffle furnace at 500°C for 30 min; the temperature was further increased from 500°C to 815°C during the next 30 min and maintained until constant weight was obtained. The percentage ash was then calculated using eq. (3). Fixed carbon was obtained after deducting the sum of moisture, ash and volatile matter contents (expressed as per cent) from 100 and calculated using eq. (4). The experiment was carried out in N_2 atmosphere.

$$\%\ \text{Moisture} = \frac{100\ (\text{Loss in weight after drying})}{\text{Total weight of sample taken}}. \tag{1}$$

$$\%\ \text{Volatile matter} = \left(\frac{100\ (\text{Loss in weight after heating})}{\text{Total weight of sample taken}}\right) - \%\ \text{Moisture}. \tag{2}$$

$$\%\ \text{Ash} = \left(\frac{100\ (\text{Weight of ash obtained after heating})}{\text{Total weight of sample taken}}\right). \tag{3}$$

$$\text{Fixed carbon} = 100 - (\%\ \text{Moisture} + \%\ \text{Voltile matter} + \%\ \text{Ash}). \tag{4}$$

Determination of point of zero charge

The 'point of zero charge (pH_{pzc})' is defined as the pH at which the surface has zero net charge[16]. pH_{pzc} was determined using a 50 ml solution of 0.1 N KNO_3. The initial pH (pH_i) of the solution was adjusted between 2 and 12 by adding either 0.1 M HCl or 0.1 M NaOH solution. About 0.5 g of FVP sample was added to a series of bottles containing solutions of different pH values. These bottles were agitated for 48 h at 30°C. The final pH (pH_f) was measured for each bottle. When plotting a graph of $\Delta pH(pH_i - pH_f)$ versus pH_i, the point at which the curve cuts the line (i.e. $pH_i = pH_f$) is defined as 'pH_{pzc}'[17].

Determination of surface charges and surface pH

The surface acidity and basicity of FVP were determined using the titration method[17].

Surface acidity: Surface acidity was determined by adding 0.5 g of FVP to 50 ml of 0.01 N NaOH. The samples were shaken at 30°C for 24 h in a thermostatic shaker. The mixture was then filtered and finally back titrated with 0.01 N HCl. The amount of acidic groups available on FVP was determined from the end point, and finally the number of acid sites available was expressed in mmol/g of FVP.

Surface basicity: The total surface basicity was determined by mixing 0.5 g of the FVP sample with 50 ml of 0.1 N HCl solution. The mixture was shaken for 24 h at 30°C. An aliquot of the supernatant was then filtered and back titrated with 0.1 N NaOH to determine the end point, and finally the number of basic sites available was expressed in mmol/g of FVP.

Surface pH: About 1 g of FVP was mixed in 50 ml of double-distilled water and shaken in a thermostatic shaker at 30°C. After 24 h, the mixture was filtered and its final pH was determined, which gives the surface pH.

Particle density, bulk density, porosity and water absorption capacity of FVP

The particle density, bulk density and porosity of FVP particles were determined by applying the tap density method. 'Water absorption capacity' is the capability of FVP to hold water. To determine the water absorption capacity, 1 g of FVP was added to 50 ml of double-distilled water. The mixture was allowed to react for 3 h, following which the residual water was decanted and measured. The difference between the final and initial volumes of water gives the water holding capacity of FVP.

Results and discussion

Proximate and ultimate analyses

Table 1 presents the results of proximate and ultimate analyses of FVP. FVP can be easily stockpiled for a longer period because it is resistant to mould growth, as it has a low moisture percentage (5–10)[18]. The organic nature of FVP is confirmed by higher volume of volatiles (83–90%). This organic matter mainly includes proteins, carbohydrates and lipids, all of which are a good source of nutrients. FVP contains incombustible solid materials (2–9%) in the form of ash. This ash is a good source of minerals and micronutrient[19]. FVPs are easier to ignite and burn, and can attain their maximum combustion temperature; however, this process is difficult to control due to its low moisture and high volatile matter content.

During combustion, due to high volatile matter composition, devolatilization is usually performed at low temperatures. The volatile matter released following combustion mainly consists of CO, H_2 and C_xH_y. Therefore, for the operation and design of these combustion systems, combustion temperature and release of volatiles are important factors to be considered. Because the compositions of FVP vary, it is difficult to design such combustion systems[18,20].

FVPs contain 0.65–2.2% nitrogen and 37–40% carbon, making them an ideal alternative for enzyme-production processes, as a substrate with good C/N ratio favours fungal growth.

FVP contains 51–58% of oxygen, which confirms the presence of fibre and carbohydrate. Higher amounts of cellulose, hemicellulose and polymers make FPV a potential bioadsorbent for the removal of organic and inorganic pollutants from waste streams[3].

Porosity, particle density, bulk density and water absorption capacity

Table 2 presents the physical properties such as porosity, particle density, bulk density and water absorption capacity of FVP. As summarized in Table 2, the bulk density of various FVPs is in the following order: PP (0.62 g/cm^3) > PAP (0.52 g/cm^3) > WMP (0.43 g/cm^3) > PIP (0.40 g/cm^3) > GPP (0.31 g/cm^3) > GP (0.22 g/cm^3). The porosity of PIP is highest among all the FVPs studied. The bulk density of FVPs varies according to the differences in particle size or shape, or both[21].

Among the various FVPs, water absorption capacity is higher for WMP (11.5 ml/g) and GP (11.2 ml/g), while it is lowest for PIP (5.5 ml/g) (Table 2). With an increase in porosity, the volume of the entrapped air also increases. The hydrophilic groups in the fibres of FVP are responsible for the high water absorption capacity. However, because of the low density and high adsorption capacity of these materials, there are a few inherent disadvantages. The low density of FVPs causes problems during transportation, storage, processing and heating[18], whereas the high absorption capacity increases their weight, which is problematic during transportation and handling.

Table 1. Proximate and ultimate analyses of FVP

	Proximate analysis				Ultimate analysis				
FVP	% Moisture	% Ash	% Volatile matter	% Fixed carbon	% N	% C	% H	% S	% O (by difference)
PP	10.43	3.63	85.68	0.25	0.65	35.96	4.92	0.09	58.38
PAP	8.86	6.55	83.77	0.83	1.07	36.46	6.01	0.18	56.28
WMP	8.19	6.18	85.36	0.27	2.23	39.69	6.23	0.33	51.52
GP	5.84	8.47	84.94	0.75	0.65	34.48	5.70	0.26	58.91
GPP	5.96	4.24	89.20	0.60	1.90	37.70	6.19	0.14	54.07
PIP	5.53	1.95	90.70	1.83	1.23	40.90	6.13	0.14	51.60

Table 2. Physical properties of FVP

FVP	Bulk density (g/cc)	Particle density (g/cc)	Porosity (%)	Water-absorption capacity (ml/g)
PP	0.62	0.89	30.88	6
PAP	0.52	1.60	67.25	8.5
WMP	0.43	1.09	68.66	11.5
GP	0.22	0.51	56.73	11.2
GPP	0.31	0.80	61.86	8.2
PIP	0.40	1.72	76.49	5.5

Table 3. Surface charge of FVP

	Available sites		
FVP	Acidic (A)	Basic (B)	Ratio of basic sites/ acidic sites (B/A)
PP	4.05	2.25	0.56
PAP	2.25	1.5	0.67
WMP	2.3	1.65	0.72
GP	2.9	1.95	0.67
GPP	2.1	1.8	0.86
PIP	1.85	1.55	0.84

Surface charges

The nature of FVP surface can be evaluated by calculating the net amount of basic and acidic sites on it. Based on the net surface charges, the type of impurity that could be adsorbed can be determined. For determining net surface charges, the ratio of basic to acidic sites (B/A) is presented in Table 3.

From the table, it is clear that all the FVPs studied, except PAP, have more acidic sites. Among all FVPs studied, GPP has more basic sites. In GPP, the number of basic sites is almost equal to that of acidic sites (B/A = 0.86). Thus, it can be used for the removal of both cationic and anionic types of impurity. The order of surface acidity for the studied materials is as follows: PP (0.56) > PAP (0.67)/GP (0.67) > WMP (0.72) > PIP (0.84) > GPP (0.86). Thus, any FVP containing more acidic sites can be a good adsorbent for cationic pollutants such as heavy metal ions and cationic dyes (Table 4)[22–34].

If B/A > 1, then the surface has more basic (negative) charges.

If B/A = 1, then the net acidic and basic charges present is equal (neutral).

If B/A < 1, then the surface has more acidic (positive) charges.

Point of zero charge (pH_{pzc}) and surface pH

pH_{pzc} is an important factor in adsorption studies. It provides information about the degree of ionization on the adsorbent surface and its interactions with the adsorbate. In the batch equilibration studies for pH_{pzc} determination of FVP, the hydroxyl groups (OH^-) and protons (H^+) are possible determinants. The particles of FVP adsorb OH^-/H^+ from the aqueous medium. Additional protons from the solution can be either accepted or donated by the functional groups on the surface of FVP. The net charge on FVP surface depends on the solution pH. The surface of FVP becomes positive if it accepts the protons from the acidic solution, or negative if it loses protons to the basic solution. The pH at which the surface of FVP is neutral is represented as pH_{pzc} (ref. 16).

Surface pH is the property of FVP that provides information about the change in pH of water when a known amount of FVP is added to it. The pH changes due to leaching of some compounds from the surface of FVP to the solution. This property helps determine the final pH of the solution. The surface pH of PP, PAP, WMP, GP, GPP and PIP was found to be 4.17, 3.49, 4.66, 3.94, 6.09 and 5.61 respectively.

Figure 1 *a* shows the pH_{pzc} values determined in a solution of 0.01 N KNO_3, while Figure 1 *b* shows the same for double-distilled water. Table 5 presents the surface pH values of various FVPs. The pH_{pzc} values of PP, PAP, WMP, GP, GPP and PIP are 4.05, 3.29, 5.07, 3.64, 6.03 and 5.5 respectively, in DDW, whereas they are 3.91, 4.38, 5.68, 3.85, 5.96 and 5.81 respectively, in 1 N KNO_3. The pH_{pzc} values of all FVPs in both electrolyte solutions (KNO_3 and DDW) are less than 6, suggesting that the studied FVPs have more acidic groups on their surface. This is also confirmed by the B/A ratio and values of surface pH. Thus, it can be concluded that FVPs are more likely to be

Table 4. Use of FVP as adsorbent

Peel	Adsorbate	Cationic/ anionic	Activation process/agent	Q_m (mg/g)	Reference
PP	Ni	Cationic	Thermally activated at 600 ± 5°C for 1 h in the presence of air.	52	33
PP	Fe^{2+}	Cationic	Dried PP was thermally activated in a furnace at 500°C for 1 h in the absence of air. The ash was removed after activation by washing PP with 0.1 M HCl solution and distilled water, and then dried.	18.52	34
PP	Pb^{2+}	Cationic		13.87	6
	Cu^{2+}	Cationic		13.18	
	Pb^{2+}	Cationic	PP was placed in a muffle furnace for 1 h at 500°C	13.98	
	Cu^{2+}	Cationic		18.05	
	Pb^{2+}	Cationic	Soaked for 24 h in a solution of phosphoric acid and zinc chloride (1 : 1), and then dried and carbonized.	17.63	
	Cu^{2+}	Cationic		19.19	
	Pb^{2+}	Cationic	Soaked for 24 h in nitric acid (10 wt%), and then dried and carbonized as mentioned.	17.95	
	Cu^{2+}	Cationic		21.97	
PP	Methylene blue	Cationic	–	36.36	35
PP	Ca^{2+} Mg^{2+}	Cationic	PP was washed with 0.1 M HCl, rinsed with deionized water and dried in an oven at 60°C for 24 h.	28.82	36
PAP	Methylene blue	Cationic	–	97.09	7
PAP	Zn^{2+}	Cationic	–	0.45	37
GPP	Methylene blue	Cationic	Subjected to pyrolysis at 800°C for 30 min in an atmosphere of N_2 with 50% H_2SO_4 [V/V] for 24 h activation.	178.25	38
GP	Methylene blue	Cationic	–	142.86	12
GP	F^{+}	Cationic	Loaded with zirconium (IV).	20.89 16.90	39
GP	Pb^{2+}	Cationic	–	209	40
	Cu^{2+}	Cationic		37	
	Ni^{2+}	Cationic		32	
GP	Cd^{2+}	Cationic	–	51.73	13
			10 g of dried GP was treated with 200 ml (200 g/l) NaOH for 4 h at 25°C. Then, it was filtered and washed with distilled water up to pH 7.	109.05	
GP	Cu^{2+}	Cationic	50 g of GP was added to 4 g of NaOH solid reagent dissolved in 50 ml water. The mixture is intensively stirred at room temperature for 1 day to facilitate saponification.	45.75	41
	Fe^{3+}	Cationic		67.01	
	Zn^{2+}	Cationic		32.66	
	Pb^{2+}	Cationic		207.2	
	Cd^{2+}	Cationic		68.57	
GP	Cu^{2+}	Cationic	–	76.9	42
WMP	Cu	Cationic	–	5.73	43
WMP	Methylene blue	Cationic	–	250	44
PIP	Ni^{2+}	Cationic	PP was pretreated with 1 M NaOH, washed with deionized water and dried in an oven at 60°C for 6–8 h	19.23	14
PIP	Cu^{2+}	Cationic	Dried PIP was carbonized in a muffle furnace at 500°C for 1 h. The ash was removed by washing PP with 0.1 M HCl solution and distilled water until the pH reached above 5 and then dried.	3.74	45

used for the adsorption of cationic than anionic pollutants. By contrast, GPP and PIP have pH_{pzc} and surface pH values close to neutral. Therefore, they can be used for the removal of both cationic and anionic contaminants. Table 4 summarizes the contaminants adsorbed on FVP. The data presented suggest that FVPs are more suitable for the removal of cationic impurities from aqueous solution, even if different modification methods are used.

BET surface area

The BET surface area of PP, PAP, WMP, GP, GPP and PIP is 1.28, 1.00, 1.44, 1.40, 1.02 and 1.04 m^2/g respectively. This low surface area of FVP is a characteristic of carbonaceous materials[22]. Sometimes, the operational complexity involved in degassing lignocellulosic samples, results in low surface area[3].

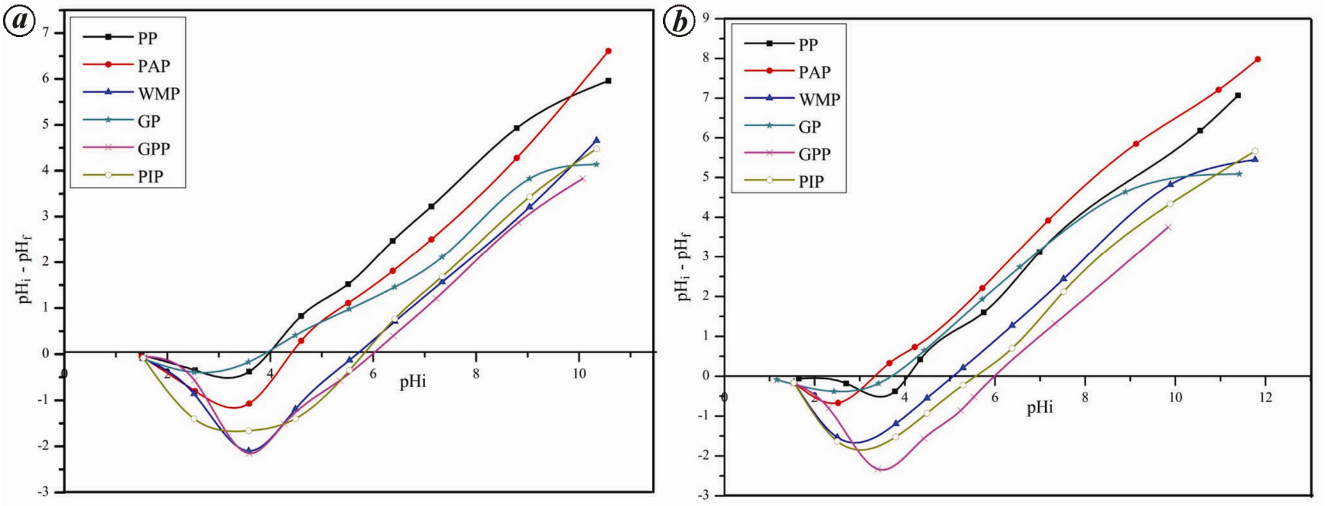

Figure 1. Point of zero charge of FVP in (***a***) 0.1 N KNO_3 solution and (***b***) double-distilled water.

Table 5. pH_{pzc} and surface pH of FVP

FVP	Point of zero charge DDW	Point of zero charge 0.1 N KNO_3	Surface pH
PP	4.05	3.91	4.17
PAP	3.29	4.38	3.49
WMP	5.07	5.68	4.66
GP	3.64	3.85	3.94
GPP	6.03	5.96	6.09
PIP	5.5	5.81	5.61

DDW, Double distilled water.

Fourier transform infrared spectroscopy

Functional groups present on the surface of FVP are important and these can be determined using FTIR. Figure 2 shows the FTIR spectra of the studied FVPs, which confirm the presence of amines, alcohol, carboxylic acid, hydroxyl, phenol, alkanes, amino acids, alkyl halide and aromatic compounds in the peels.

For PP, the stretching absorption peak centred at 3327.11 cm^{-1} can be attributed to the NH or OH groups. The band observed at about 2923.01 cm^{-1} is assigned to stretching vibrations of $–CH_3$ or $–CH_2$ groups of carboxylic acid and its bending vibration is seen at around 1319.11 cm^{-1}. The band at 2678.11 cm^{-1} represents the C–H group of alkanes. The peak at 1619.12 cm^{-1} is attributed to the C=C stretch of alkene, aromatic or N–H group of amino acids. The carbonyl stretching peak of aldehyde is observed at 1730.11 cm^{-1}. The peaks at 1234.12, 1039 and 769.12 cm^{-1} suggest the presence of tertiary alcohol or phenol, C–O stretch, and primary amine and CN stretch respectively.

For PAP, the stretching absorption peak centred at 3358.84 and 3117.95 cm^{-1} indicates the presence of NH or OH groups. The band at 2887.82 cm^{-1} is assigned to stretching vibrations of the O–H stretch of carboxylic acid and its bending vibration is seen at around 1399.11 cm^{-1}. The band at 2782.84 cm^{-1} represents the C–H group of alkanes. The peak at 1628.90 cm^{-1} represents the C=C stretch of aromatic, alkene or N–H group of amino acids. The carbonyl stretching peak of aldehyde is obtained at 1737.82 cm^{-1}. The peaks at 1237.79, 1051.71 and 754.90 cm^{-1} represent the tertiary alcohol/phenol, C–O stretch, and primary amine and C–N stretch respectively.

For WMP, the stretching absorption peak centred at 3418 and 3128.11 indicates the presence of NH or OH groups. The peak observed at 2850.78 cm^{-1} is assigned to stretching vibrations of the O–H stretch of carboxylic acid and its bending vibration is around 1400.12 cm^{-1}. The C–H group of alkanes is represented by a band at 2785.83 cm^{-1}. The C=C stretch of aromatic, alkene or N–H group of amino acids is confirmed by the band at 1692.96 cm^{-1}. The peak at 1737.82 cm^{-1} is assigned to the carbonyl stretching peak of aldehyde. The peaks at 1230.82, 1049.71 and 795.97 cm^{-1} represent phenol/tertiary alcohol, C–O stretch, and primary amine and C–N stretch respectively.

For GP, the stretching at 3440.79 and 3114.10 cm^{-1} indicates NH or OH groups. The bands at 2885.76 and 1401.12 cm^{-1} are assigned to stretching and bending vibrations of O–H of carboxylic acid respectively. The band at 2785.80 cm^{-1} is assigned to the C–H group of alkanes. The carbonyl stretching peak of aldehyde is observed at 1742.79 cm^{-1}. The peaks at 1238.78, 1045.69 and 795.97 cm^{-1} represent the phenol/tertiary alcohol, C–O stretch, and primary amine and C–N stretch respectively.

For GPP, the stretching peak at 3321.12 cm^{-1} represents the OH group of alcohol. The bands at 2919.11 and 1319.11 cm^{-1} are assigned to stretching and bending

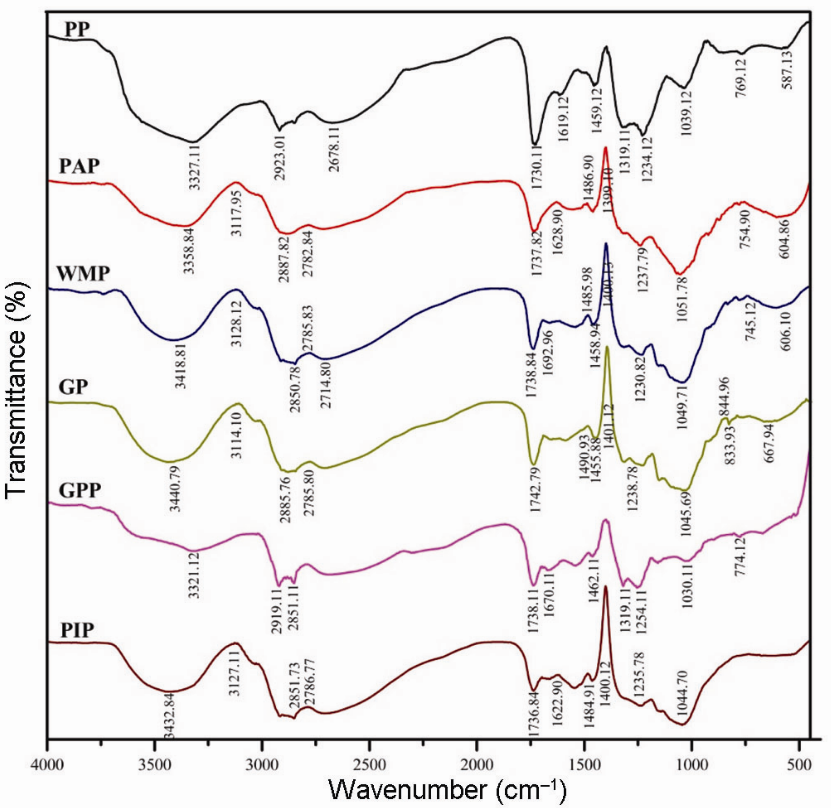

Figure 2. FTIR spectra of FVP.

vibrations of the O–H group in carboxylic acid respectively. The C–H of alkanes is confirmed by the band at 2851.11 cm^{-1}. The C=C stretch of aromatic, alkene or N–H group of amino acids is confirmed by the band at 1670.11 cm^{-1}. The peak at 1738.11 cm^{-1} represents the carbonyl stretching peak from aldehyde. The peaks at 1254.11, 1030.12 and 774.12 cm^{-1} represent phenol/tertiary alcohol, C–O stretch, and primary amine and C–N stretch respectively.

For PIP, the stretching peak centred at 3432.84 and 3127.10 cm^{-1} confirms the NH or OH groups. The peaks observed at 2851.73 and 1400.13 cm^{-1} are allocated to stretching and bending vibrations of carboxylic acid. The C–H of alkanes is signified by a band at 2786.77 cm^{-1}. The C=C stretch of aromatic, alkene or N–H group of amino acids is represented by the band at 1622.90 cm^{-1}. The peak at 1736.84 cm^{-1} is assigned to the carbonyl stretching band of aldehyde. The peaks at 1235.78 and 1049.71 cm^{-1} represent phenol/tertiary alcohol and C–O stretch and primary amine respectively.

The presence of carboxylic acid makes FVP a pharmaceutically useful product. In addition, carboxylic acid makes the material suitable for adsorption of metals. Pectin, cellulose or lignin are the main sources of carboxylic acid in FVP[23,24]. The hydroxyl and polyphenolic groups in FVP are useful for the adsorption of anionic impurities such as dyes[25]. The peak between 2220 and 2260 cm^{-1} is absent in FVP, which indicates the nonexistence of cyanide groups. This makes FVP a nontoxic material for further use[36].

Scanning electron microscopy

The particle structure and geometry of the FVP surface were identified by scanning electron microscopy. The SEM result indicates that the surface of FVP is rough, bumpy and flex. Some macropores and micropores are also present on the surface.

The surface of PP is rough and uneven (Figure 3 *a*) with some pores. In contrast, PAP has a rough surface without pores (Figure 3 *b*). WMP has a lopsided surface with negligible and small pores (Figure 3 *c*). The surface of GP is asymmetrical and is less porous (Figure 3 *d*). The surface of GPP is bumpy with long flakes (Figure 3 *e*), while the surface of PIP is rough and irregular (Figure 3 *f*). In general, the high surface area of solid particles is due to the presence of pores on the surface. From the SEM images, it is clear that less number of pores is present on the surface of FVP, and therefore, the BET surface area of the studied FVPs is less as discussed earlier.

Thermal analysis

The thermal stability of FVP was determined by TG and DTG analysis, which was carried out at a heating rate of

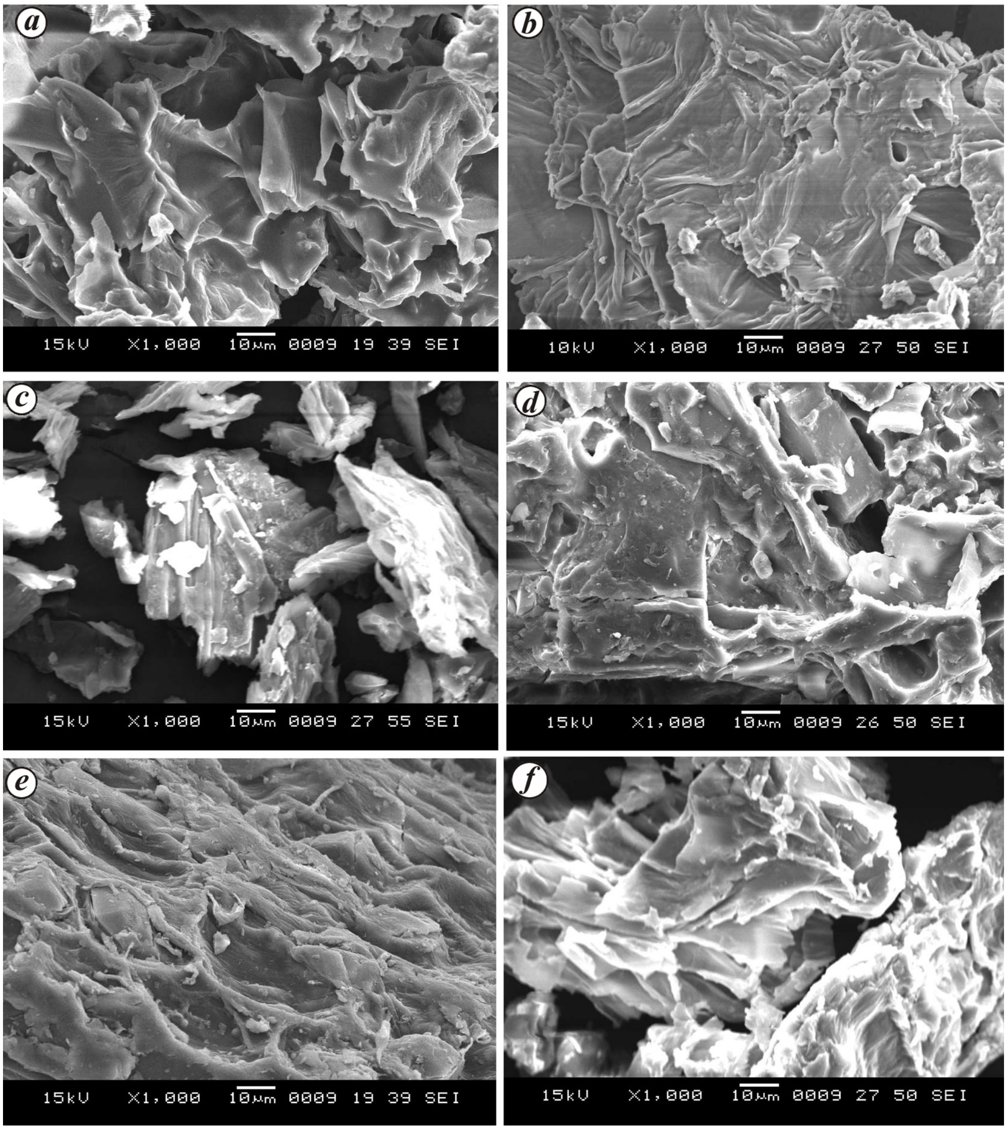

Figure 3. SEM images of (***a***) pomegranate, (***b***) pineapple, (***c***) watermelon, (***d***) garlic, (***e***) green pea and (***f***) pigeon pea.

30°C/min under an atmosphere of nitrogen. Figure 4 *a* shows the TG curves of FVP. The first weight loss region in this curve can be seen between 200°C and 300°C, which is due to the removal of some volatile organic materials (oils, terpenes, pigments, etc.) and moisture from FVP, which constitute approximately 85% and 8% of the total weight respectively. The second weight loss region is observed at 150–400°C, and this corresponds to decomposition of cellulose and hemicellulose. Beyond 400°C, weight loss is very slow due to the presence of fixed carbon, which is more stable at higher temperatures. Results of proximate analysis indicate that up to 2% of fixed carbon is present in FVP.

Figure 4 *b* shows the DTG curves of FVP. The major decomposition peaks are observed between 200°C and 250°C as well as 300°C and 400°C. The first decomposition peak confirms the presence of hemicellulose and pectin in FVP. The second peak corresponds to the decomposition of cellulose. The flat tailing portion of the DTG curves at higher temperatures signifies the presence of fixed carbon and lignin, which decompose slowly over a wide range of temperatures.

The decomposition temperature of FVP is between 200°C and 250°C, which is much lower than that of bituminous coal (350°C). This shows that FVPs are combustible at lower temperatures compared to coal[26–30]. Below 150°C, however, FVP is stable and can be used as an adsorbent in its natural form.

Potential applications of FVP

We envisaged the potential use of FVP as a biosorbent after carrying out several physico-chemical characterization

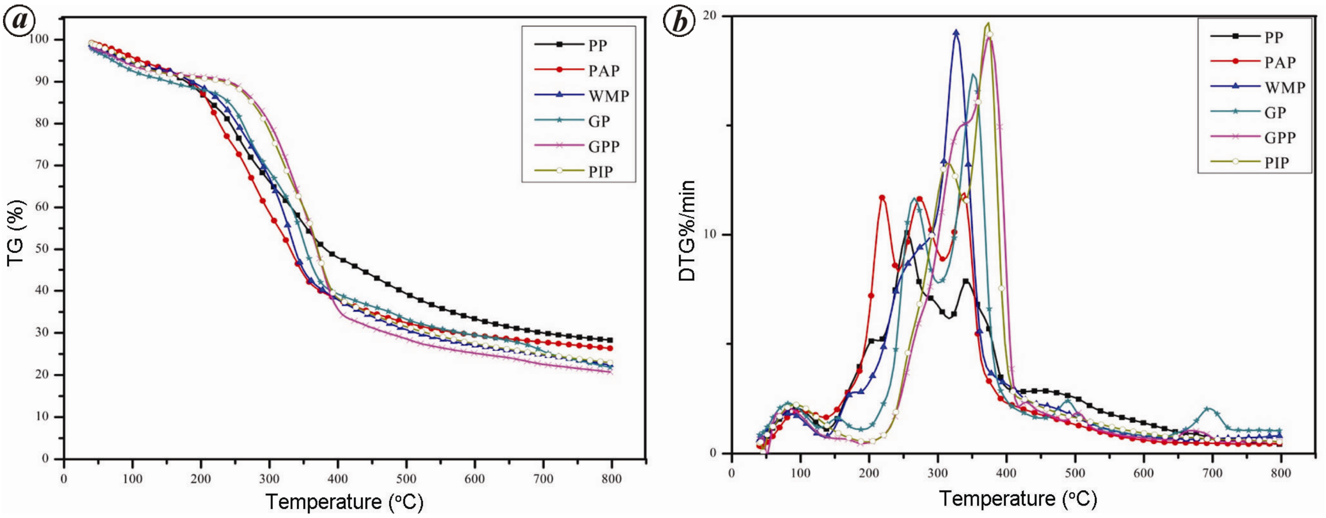

Figure 4. (*a*) Thermogravimetric (TG) and (*b*) derivative of thermogravimetric (DTG) spectra of FVP.

studies. The surface properties of FVPs indicate that these materials have more acidic sites, low BET surface area, and different functional groups with rough and porous surface. This blend of properties makes FVP a suitable biosorbent. For example, adsorption of heavy metals, dyes and organic impurities from aqueous solution on FVP has shown promising results. For this purpose, FVP can be used in its natural or modified form, or as activated carbon (Table 4)[31].

The results of proximate and ultimate analyses indicate that FVP is rich in volatiles, H and C, and moisture content, but has lower ash content. TG/DTG analysis indicates that FVP can be decomposed at lower temperature[32].

Conclusion

In this study, we have presented the physico-chemical properties of FVPs in detail for an in-depth understanding of each FVP and its potential reutilization as an adsorbent. The surface pH and pH_{pzc} values of all FVPs suggest that they contain more number of acidic groups, and thus can be used for the removal of cationic pollutants more efficiently. In addition, GPP (0.86) and PIP (0.84) have B/A ratio close to 1, indicating that these two FVPs have both acidic and basic groups in equal amounts, enabling them to remove both cationic and anionic impurities. The BET surface area of FVP is low, but its surface is irregular and rough with some pores. FTIR results confirm the presence of different functional groups such as phenol, alcohol, carboxylic acid, alkanes, amines, amino acids and aromatic alkyl halide in each FVP. In thermal analysis, maximal weight loss is observed in the 150–400°C range, which is mainly due to decomposition of hemicellulose, cellulose and lignin. Below 150°C, FVPs are thermally stable. This physico-chemical characterization enables the reutilization of FVP as a low-cost adsorbent.

1. Patel, S., Potential of fruit and vegetable wastes as novel biosorbents summarizing the recent studies. *Rev. Environ. Sci. Biotechnol.*, 2012, **11**, 365–380.
2. Midha, S., Horticulture Statistics in India, 2012, pp. 148–161.
3. Palma, C., Contreras, E., Urra, J. and Martınez, M. J., Eco-friendly technologies based on banana peel use for the decolourization of the dyeing process wastewater. *Waste Biomass Valorization*, 2011, **2**, 77–86.
4. Ay, C. O., Ozcanm, A. S., Erdogan, Y. and Ozcan, A., Characterization of *Punica granatum* L. peels and quantitatively determination of its biosorption behavior towards lead(II) ions and acid blue 40. *Colloids Surf. B*, 2012, **100**, 197–204.
5. Bhatnagar, A., Sillanpää, M. and Witek-Krowiak, A., Agricultural 'waste peels' as versatile biomass for water purification – a review. *Chem. Eng. J.*, 2015, **270**, 244–271.
6. El-Ashtoukhy, E.-S.Z., Amina, N. K. and Abdelwahab, O., Removal of lead(II) and copper(II) from aqueous solution using pomegranate peel as a new adsorbent. *Desalination*, 2008, **223**, 162–173.
7. Krishni, R. R., Foo, K. Y. and Hameed, B. H., Food cannery effluent, pineapple peel as an effective low-cost biosorbent for removing cationic dye from aqueous solutions. *Desalination Water Treatment.*, 2014, **52**, 6096–6103.
8. Bardiya, N., Somayaji, D. and Khanna, S., Biomethanation of banana peel and pineapple waste. *Bioresour. Technol.*, 1996, **58**, 73–76.
9. Foo, L. P. Y., Tee, C. Z., Raimy, N. R., Hassell, D. G. and Lee, L. Y., Potential Malaysia agricultural waste materials for the biosorption of cadmium(II) from aqueous solution. *Clean Technol. Environ. Policy*, 2011, **14**, 273–280.
10. Lakshmipathy, R. and Sarada, N. C., Adsorptive removal of basic cationic dyes from aqueous solution by chemically protonated watermelon (*Citrullus lanatus*) rind biomass. *Desalination Water Treatment*, 2013, **167**(6), 1–10.
11. Liu, C., Ngo, H. H. and Guo, W., Watermelon rind: agro-waste or superior biosorbent? *Appl. Biochem. Biotechnol.*, 2012, **167**, 1699–1715.
12. Hameed, B. H. and Ahmad, A. A., Batch adsorption of methylene blue from aqueous solution by garlic peel, an agricultural waste biomass. *J. Hazard. Mater.*, 2009, **164**, 870–875.
13. Liu, W., Liu, Y., Tao, Y., Yu, Y., Jiang, H. and Lian, H., Comparative study of adsorption of Pb(II) on native garlic peel and mercerized garlic peel. *Environ. Sci. Pollut. Res.*, 2014, **21**, 2054–2063.

14. Aravind, J., Muthusamy, S., Sunderraj, S. H., Chandran, L. and Palanisamy, K., Pigeon pea (*Cajanus cajan*) pod as a novel eco-friendly biosorbent: a study on equilibrium and kinetics of Ni(II) biosorption. *Int. J. Ind. Chem.*, 2013, **4**, 1–9.
15. Standard, I., *Methods of Test for Coal and Coke PART I: Proximate Analysis (Second Revision)*, IS: 1350, fourth reprint, July 2006.
16. Cerovic, L. S., Milonjic, S. K., Todorovic, M. B., Trtanj, M. I., Pogozhev, Y. S., Blagoveschenskii, Y. and Levashov, E. A., Point of zero charge of different carbides. *Colloids Surf. A*, 2007, **297**, 1–6.
17. Al-Degs, Y., Khraisheh, M. A. M., Allen, S. J. and Ahmad, M. N., Effect of carbon surface chemistry on the removal of reactive dyes from textile effluent. *Water Res.*, 2000, **34**, 927–935.
18. Werthera, J., Saengera, M., Hartgea, E.-U., Ogadab, T. and Siagib, Z., Combustion of agricultural residues. *Prog. Energy Combust. Sci.*, 2000, **26**, 1–27.
19. Anhwange, B. A., Chemical composition of *Musa sapientum* (banana) peels. *J. Food Technol.*, 2008, **6**, 263–266.
20. Jenkins, B. M., Baxter, L. L., Miles Jr, T. R. and Miles, T. R., Combustion properties of biomass. *Fuel Proc. Technol.*, 1998, **54**, 17–46.
21. Presley, M. A. and Christensen, P. R., The effect of bulk density and particle size sorting on the thermal conductivity of particulate materials under Martian atmospheric pressures. *J. Geophys. Res.*, 1997, **102**, 9221–9229.
22. Castro, R. S. D. *et al.*, Banana peel applied to the solid phase extraction of copper and lead from river water: preconcentration of metal ions with a fruit waste. *Ind. Eng. Chem. Res.*, 2011, **50**, 3446–3451.
23. Nair, L. D., Sar, S. K., Arora, A. and Mahapatra, D., Fourier transform infrared spectroscopy analysis of few medicinal plants of Chhattisgarh, India. *J. Adv. Pharm. Edu. Res.*, 2013, **3**, 196–200.
24. Schiewer, S. and Patil, S. B., Pectin-rich fruit wastes as biosorbents for heavy metal removal: equilibrium and kinetics. *Bioresour. Technol.*, 2008, **99**, 1896–1903.
25. Gong, R., Zhang, X., Liu, H., Sun, Y. and Liu, B., Uptake of cationic dyes from aqueous solution by biosorption onto granular kohlrabi peel. *Bioresour. Technol.*, 2007, **98**, 1319–1323.
26. Heikkinen, J. M., Hordijk, J. C., Jong, Wd. and Spliethoff, H., Thermogravimetry as a tool to classify waste components to be used for energy generation. *J. Anal. Appl. Pyrol.*, 2004, **71**, 883–900.
27. Chen, B. and Chen, Z., Sorption of naphthalene and 1-naphthol by biochars of orange peels with different pyrolytic temperatures. *Chemosphere*, 2009, **76**, 127–133.
28. Zou, W. H., Zhao, L. and Zhu, L., Efficient uranium(VI) biosorption on grapefruit peel: kinetic study and thermodynamic parameters. *J. Radioanal. Nucl. Chem.*, 2012, **292**, 1303–1315.
29. Umamaheswaran, K. and Batra, V. S., Physico-chemical characterization of Indian biomass ashes. *Fuel*, 2008, **87**, 628–638.
30. Ghani, W. A. W. A. K., Abdullah, M. S. F., Matori, K. A., Alias, A. B. and Silva, Gd., Physical and thermochemical characterization of Malaysian Biomass Ashes, *The Institution of Engineers, Malaysia*, 2010, **71**, 9–18.
31. Pathak, P. D., Mandavgane, S. A. and Kulkarni, B. D., Fruit peel waste as a novel low-cost bio adsorbent. *Rev. Chem. Eng.*, 2015, **31**, 361–381.
32. Patel, B. and Gami, B., Biomass characterization and its use as solid fuel for combustion. *Iran. J. Energy Environ.*, 2012, **3**, 123–128.
33. Bhatnagar, A. and Minocha, A. K., Biosorption optimization of nickel removal from water using *Punica granatum* peel waste. *Colloids Surf. B*, 2010, **76**, 544–548.
34. Moghadam, M. R., Nasirizadeh, N., Dashti, Z. and Babanezhad, E., Removal of Fe(II) from aqueous solution using pomegranate peel carbon: equilibrium and kinetic studies. *Int. J. Indust. Chem.*, 2013, **4**, 1–6.
35. Güzel, F., Aksoy, Ö. and Akkaya, G., Application of pomegranate (*Punica granatum*) pulp as a new biosorbent for the removal of a model basic dye (methylene blue). *World Appl. Sci. J.*, 2012, **20**, 965–975.
36. Ashraf, M. A., Maah, M. J., Yusoff, I., Mahmood, K. and Wajid, A., Study of biosorptive potential in the peel of *Citrus reticulata*, *Punica granatum*, *Daucus carota* and *Momordica charantia*. *Afr. J. Biotechnol.*, 2011, **10**, 15364–15371.
37. Mishra, V., Balomajumder, C. and Agarwal, V. K., Biosorption of Zn(II) onto the surface of non-living biomasses: a comparative study of adsorbent particle size and removal capacity of three different biomasses. *Water Air Soil Pollut.*, 2010, **211**, 489–500.
38. Dod, R., Banerjee, G. and Saini, S., Adsorption of methylene blue using green pea peels (*Pisum sativum*): a cost-effective option for dye-based wastewater treatment. *Biotechnol. Bioprocess Eng.*, 2012, **17**, 862–874.
39. Kai, H., Jiu-Gang, S., Hong-Min, Z. and Katsutoshi, I., Removal of fluoride from aqueous solution onto Zr-loaded garlic peel (Zr-GP) particles. *J. Central South Univ. Technol.*, 2011, **18**, 1448–1453.
40. Liang, S., Guo, X. and Tian, Q., Adsorption of Pb^{2+}, Cu^{2+} and Ni^{2+} from aqueous solutions by novel garlic peel adsorbent. *Desalination Water Treatment*, 2013, **51**, 7166–7171.
41. Huang, K., Jiao, S. and Zhu, H., Removal of cadmium from aqueous solution by garlic peel. In International Conference on Materials for Renewable Energy and Environment, 19–21 August 2013.
42. Chowdhury, A., Bhowal, A. and Datta, S., Equilibrium, thermodynamic and kinetic studies for removal of copper(II) from aqueous solution by onion and garlic skin. *Water*, 2012, **4**, 37–51.
43. Liu, C., Ngo, H. H., Guo, W. and Tung, K.-L., Optimal conditions for preparation of banana peels, sugarcane bagasse and watermelon rind in removing copper from water. *Bioresour. Technol.*, 2012, **119**, 349–154.
44. Djelloul, C. and Hamdaoui, O., Removal of cationic dye from aqueous solution using melon peel as nonconventional low-cost sorbent. *Desalination Water Treatment*, 2013, **52**(40–42), 1–10.
45. Parate, V. R. and Talib, M. I., Characterization of tur dal (*Cajanus cajan*) husk carbon and its kinetics and isotherm study for removing Cu(II) ions. *IOSR J. Environ. Sci., Toxicol. Food Technol.*, 2015, **9**, 27–41.

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