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Activated carbon from jackfruit peel waste by H_3PO_4 chemical activation: Pore structure and surface chemistry characterization

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Abstract

The effects of activation temperature and impregnation ratio on the pore structure and surface chemistry of activated carbons derived from jackfruit peel with chemical activation method using phosphoric acid as activating agent were studied. Activated carbons with well-developed pore sizes were produced at activation temperatures of 450 and 550 °C. The BET surface areas and total pore volumes of the carbons produced at these temperatures are in the range of 907–1260 m^2/g and 0.525–0.733 cm^3/g, respectively.

Keywords: Activated carbon; Adsorption; Jackfruit peel; Phosphoric acid; Surface chemistry

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1. Introduction

Activated carbons are the most versatile and commonly used adsorbents because of their extremely high surface areas and micropore volumes [1], large adsorption capacities, fast adsorption kinetics, and relative ease of regeneration [2]. They are produced from a variety of carbonaceous source materials. The choice of precursor is largely dependent on its availability, cost, and purity, but the manufacturing process and intended application of the product are also important considerations [3].

Precursors used for the production of activated carbons are organic materials that are rich in carbon, such as coal, lignite, and wood. Although coal is the most commonly used precursor, agricultural waste in certain condition is a better choice [1]. Activated charcoal produced from residues would reduce the pressure on forests since wood is also commonly used for this purpose [4]. Many agricultural by-products such as coconut shell [2,4,5], grain sorghum [6], coffee bean husks [7], rubber wood sawdust [8], chestnut wood [9], and fruit stones [10], have been discovered to be suitable precursors for activated carbon due to their high carbon and low ash contents. Agricultural wastes are considered to be a very important feedstock because of especially two facts: they are renewable sources and low cost materials [3].

Jackfruit is commonly used in South and Southeast Asian cuisines. Jackfruit was originally from India and spread out into tropic regions, including Indonesia. Jackfruit is very popular to Indonesian people. It can be eaten unripe or ripe, and cooked or uncooked. Moreover, there is no in-season or out-of-season for jackfruit. Therefore, it can be harvested all year long. These things indicate high demand of jackfruit in Indonesia and automatically result in high output of jackfruit peel waste.

Recent data given by Indonesian Statistical Center Bureau shows that there is increasing production of jackfruit; calculated as variety of nangka cempedak. The values were 537, 186; 694, 654; and 710, 795 tonnes by the year of 2002, 2003, and 2004, respectively. Although only production of one variety of jackfruit was revealed, it leads to a fact that Indonesia has abundant source of jackfruit, since besides nangka cempedak Indonesia also has numerous excellent jackfruit varieties. Jackfruit peel wastes have no economic value and in fact often create a serious problem of disposal for local environments. Conversion of jackfruit peel into activated carbon would increase its economic value, help reduce the cost of waste disposal, and provide a potentially inexpensive raw material for commercial activated carbon. In this research, raw material for activated carbon was obtained by collecting jackfruit peel of one variety of jackfruit, i.e. nangka kunir, from local fruit stores at Malang, East Java. The selection of *nangka kunir* is due to its high availability of the variety in East Java.

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The activation of precursor can be carried out in two different methods, which are physical and chemical activation. In this study jackfruit peel was activated with chemical activation method using phosphoric acid as an activating agent. The advantages of chemical activation are low energy cost, since chemical activation usually takes place at a temperature lower than that used in physical activation, and yields of chemical activation are higher than physical one [11,12]. Chemical activation also has better development of a porous structure [13].

Phosphoric acid and zinc chloride are used for the activation of lignocellulosic materials, which have not been carbonized previously; whereas metal compounds such as potassium hydroxide are used for the activation of coal precursors or chars. When compared to zinc chloride, phosphoric acid is the most preferred because of the environmental disadvantages associate with zinc chloride. Problem of corrosion and inefficient chemical recovery is also associates with it. Moreover, the carbons obtained using zinc chloride cannot be used in pharmaceutical and food industries as it may contaminate the product [8]. Although potassium hydroxide develops large microporosity, yield of activated carbon impregnated by potassium hydroxide is lower than those activated with zinc chloride or phosphoric acid, and at high temperature, i.e. > ±650 °C, the carbon content is less than fixed carbon in initial precursor. The presence of metallic potassium will intercalate to the carbon matrix [12], yielding lower yield of activated carbon, less then the carbon content of the raw material.

It has been found that both the surface area and the nature of porosity are greatly influenced by the processing modes. In general, activation using phosphoric acid can be classified either as single-stage or two-stage activation process carried out either in inert medium or self-generated atmosphere. The activation process is also carried out with effort made towards developing a high surface area carbon with desired pore size by optimizing the process parameters; such as the activation time, activation temperature, and impregnation ratio. Study of various parameters by Ahmadpour and Do [14] revealed that the most important variable to porosity of activated carbon development is the ratio of the chemical agent to the precursor. The other operation variables with a direct effect on the porosity development are activation temperature and method of mixing. Nevertheless, it has been found that ordinary (sample—activating agent mixture) impregnation-method is the best method of mixing compared with physical and acid washed method [14].

According to the knowledge of the authors, there is only one publication about the usage of jackfruit peel as precursor for activated carbon production which was reported by Inbaraj and Sulochana [15]. They used sulphuric acid as activating agent and emphasized on its application on Cd (II) adsorption. Therefore, in this present study, one of well-known activating agent, i.e. phosphoric acid, was used to activate jackfruit peel.

The adsorption behavior of activated carbon is determined not only by their porous structures but also by the chemical nature of its surface. The porous structure of carbon determines its adsorption capacity, while its surface chemical groups affect its interaction with polar and non-polar adsorbates [16]. It indicates that surface chemistry has a role in adsorption process. A thorough knowledge of activated carbon surface chemistry enables preparation of adsorbent with appropriate characteristic for specific application. Thus, in this research, pore characteristic and surface chemistry are worth to be investigated by several means of characterization method because of their important roles in adsorption.

2. Experimental technique

2.1. Preparation of activated carbon

First of all, raw material of the activated carbon was acquired by collecting jackfruit variety *nangka kunir* from a local fruit store at Malang, East Java. Then, the jackfruit peel was removed and subsequently cleaned by removing the carpel fibers and washing several times with distilled water to remove impurities. The jackfruit peel was then dried at 105 °C until constant weight of the sample was reached. After that, the dried jackfruit peel was then grounded by JANKE & KUNKEL micro hammer mill. Then, dried and size-reduced jackfruit peel was kept in a desiccator as raw material for activated carbon production. The proximate analysis of the raw material used in this study was conducted using ASTM Standards and was found to be 4.22, 10.19, 50.17, and 35.42% for moisture, ash, volatile matter, and fixed carbon content, respectively.

Chemical activation method using phosphoric acid was used to activate the raw material. 20 g of raw material was impregnated by certain amount of 85 wt.% concentration phosphoric acid with occasional stirring. The amount of phosphoric acid solution used was adjusted to give a certain impregnation ratio (weight of activating agent/weight of raw material) of 1:1, 2:1, 3:1, and 4:1. The resulting slurry was then kept in a desiccator overnight.

After 24 h, the slurry was then ready to have two-stage activation process with semi-carbonization as first stage [8]. In the first stage, the slurry was put in a horizontal tubular reactor and kept in a muffle furnace to experience semi-carbonization at a temperature 200 °C for 30 min. As reported by other authors [8,17,18], the mixture of the raw material and phosphoric acid then turned black, yielding black and sticky dry powder. After semi-carbonization, the black and sticky dry powder was heated until certain activation temperature was reached. The carbonization was performed under a nitrogen flow of 100 $\mathrm{cm^3\,min^{-1}}$ STP for 45 min. After activation, the activated carbon product was collected and cooled in a desiccator. The activated carbon product was then repeatedly washed with warm distilled water (70 °C) until constant pH of the solution was reached. Finally, the activated carbon was dried in a vacuum oven at 110 °C for 24 h. The activated carbon was then stored in a desiccator for later experiment use.

2.2. Physical characterization of jackfruit peel activated carbon

The pore structures of the resulting carbons were analyzed using N_2 adsorption, X-ray diffraction (XRD), and scanning electron microscope (SEM).

2.2.1. N_2 adsorption

The pore structure characteristics of the resulting carbon were determined by nitrogen adsorption at −196 °C by a Quadra-Sorb SI. Prior to gas adsorption measurements, the carbon was degassed at 200 °C in a vacuum condition for a period of at least 24 h. Nitrogen adsorption isotherms were measured over a relative pressure (P/P_o) range from approximately 0.005 to 0.985. The BET surface area was determined by means of the standard BET equation applied in the relative pressure range from 0.06 to 0.3. The total pore volume was calculated at a relative pressure of approximately 0.985 and at this relative pressure all pores were completely filled with nitrogen gas. The DFT pore size distribution of all carbon samples were obtained based on nitrogen adsorption isotherms, using Quadrachrome Quadrawin software package with medium regularization.

2.2.2. SEM

SEM images were recorded using JEOL JSM-6300F field emission SEM. A thin layer of platinum was sputter-coated on the samples for charge dissipation during FESEM imaging. The sputter coater (Eiko IB-5 Sputter Coater) was operated in an argon atmosphere using a current of 6 mA for 3 min. The coated samples were then transferred to the SEM specimen chamber and observed at an accelerating voltage of 5 kV, eight spot size, four aperture and 15 mm working distance.

2.2.3. XRD

Powder X-ray diffraction patterns were recorded on a Rigaku Miniflex Goniometer at 30 kV and 15 mA (Cu Kα radiation) at a step size of 0.01°.

2.3. Surface chemistry characterization of jackfruit peel activated carbon

The surface chemistry characterization of the activated carbon was performed with Boehm titration, pH drift and Fourier Transform Infrared Spectroscopy (FTIR) to identify its surface functional groups both qualitatively and quantitatively.

2.3.1. Boehm titration

The Boehm titration method can be described as follows: 0.5 g of activated carbon were placed to a series of flask which contain 50 ml of 0.05 N sodium bicarbonate, sodium carbonate, sodium hydroxide and hydrochloric acid. The flasks were sealed and shaken for 24 h. After 24 h, the solutions were filtered, and then 10 ml of each solution was pipetted to a flask and was titrated with 0.05 N sodium hydroxide and or hydrochloric acid, depending on the original solution used. The amount of acidic groups on the activated carbon is calculated under the assumption that NaOH neutralizes carboxylic, lactonic, and phenolic groups; Na_2CO_3, carboxylic and lactonic; $NaHCO_3$, only carboxylic group. The number of surface basic sites is calculated from the amount of HCl that reacted with the carbon. The reaction between the reagents and the acidic oxygenated-functional groups on the surface is based on the difference in acid/base strength. The strength of acidic groups is as follow: carboxyl > lactone > phenol [16].

2.3.2. pH drift method

This method was conducted to determine the pH_{PZC} of jackfruit peel activated carbon. pH_{PZC} (point of zero charge/zero charge point/zero point charge) is pH when the charge in the activated carbon surface is zero. The procedure of pH drift method can be described as follows: 50 ml of 0.01 N NaCl were prepared and added into a series of Erlenmeyer. Then, their pH values were adjusted in range between 2 and 12 with interval 0.1 using 0.01 N HCl solution and 0.01 N NaOH. pH of initial solutions were measured with pH meter and then noted as pHinitial. After constant value of pHinitial had been reached, 0.15 g of activated carbon sample was added into each Erlenmeyer and then shaken for 48 h. After 48 h, pH of solution was measured using pH meter and noted as pHfinal. pH_{PZC} of activated carbon sample is the point when pHinitial = pHfinal.

2.3.3. Infrared spectroscopy

A quantitative analysis of activated carbon was conducted by obtaining FTIR transmission spectra of carbon samples by KBr technique. The technique was conducted by placing the KBr powder grinded with an agate mortar in the sample cup and then the powder surface was evened using the attached sample pressing bar. Next, the powder was mounted to the instrument to make a background measurement. After that, the activated carbon sample was diluted with the KBr powder with the ratio of 10% and grounded with the agate mortar until it becomes fine particles to mix the both kinds. Then, the mixed powder was placed in the sample cup and the powder surface was also evened using the sample pressing bar. Finally, the mixed powder was mounted to the instrument to make a sample measurement in the transmittance %T mode. The analysis was carried out by Shimadzu 8400S FTIR instrument in wave number range of 4000–500 cm^{-1}.

3. Results and discussions

Proximate analysis of jackfruit peel is given in Table 1. This table reveals that the precursor used in this study has high carbon content approximately 35% and low ash content about 4% indicate that jackfruit peel is suitable to be used as activated carbon precursor.

3.1. Yield of activated carbon

In activated carbon preparation, yield is usually defined as final weight of activated carbon produced after activation, washing, and drying, divided by initial weight of raw material; both on a dry basis [6]. Fig. 1 shows the yield of activated carbon

Table 1
Proximate analysis of jackfruit peels

Material	Weight (%)
Ash	4
Moisture	10
Volatile matter	50
Fixed carbon	36
Total	100.00

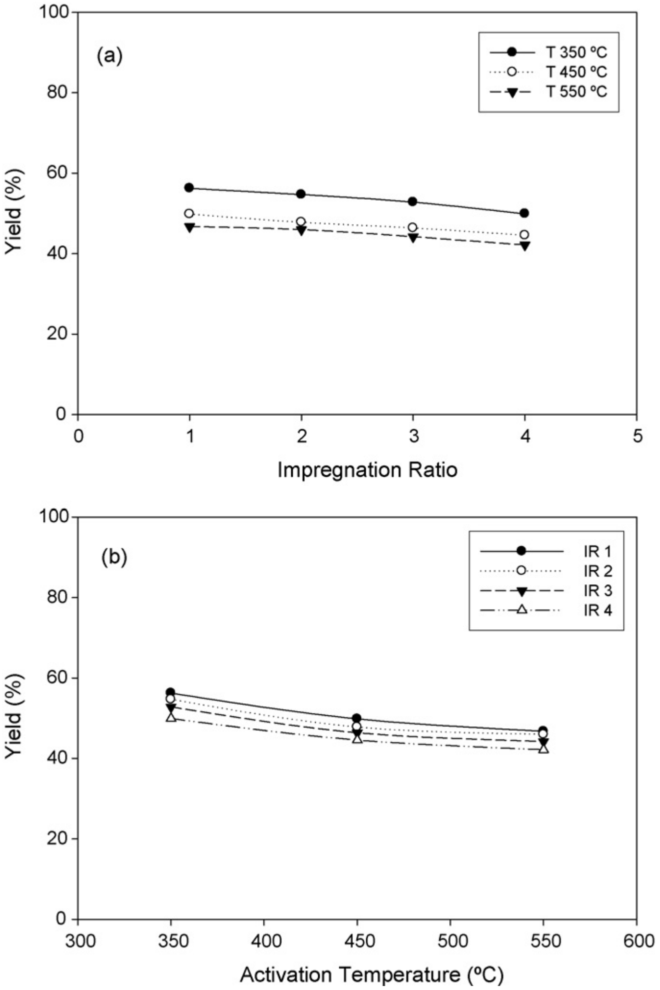

Fig. 1. Effect of (a) impregnation ratio and (b) activation temperature on yield of activated carbon.

prepared from jackfruit peel at different activation temperatures and impregnation ratio.

As indicated in Fig. 1, the yields of activated carbon obtained in this study are in the range of 42.15–56.25%. Similar results were also obtained by other studies [8–10,17], i.e.: 46–63% for activated carbon from rubber wood sawdust, 37.2–42.3% for activated carbon from chestnut wood, 31.9–48.5% for activated carbon from fruit stones, and 42–51% for activated carbon from cellulose.

The yield of activated carbon obtained by chemical activation using phosphoric acid as activating agent is higher than the fixed carbon content of raw material. Essentially, jackfruit peel is a complex composite material formed of natural polymers (cellulose, lignin, and hemicellulose). In activation or carbonization at high temperature, these polymeric structures decompose and liberate most of the non-carbon elements, mainly hydrogen, oxygen and nitrogen in the form of liquid (called as tars) and gases, leaving behind a rigid carbon skeleton in the form of aromatic sheets and strips. The presence of phosphoric acid during activation promotes depolymerization, dehydration, and redistribution of constituent biopolymers, and also favoring the conversion of aliphatic to aromatic compounds thus increasing the yield of activated carbon [19,20].

Fig. 1 depicts the effect of activation temperature and impregnation ratio on yield of activated carbon. This figure shows that the carbon yield was found to decrease with the increasing of temperature and impregnation ratio. The reaction of lignocellulosic with phosphoric acid begins as soon as the components are mixed, the acid first attacks hemicellulose and lignin because cellulose to be more resistant to acid hydrolysis [21]. Here the acid will hydrolyze glycosidic linkages in lignocellulosic and cleave aryl ether bond in lignin. These reactions are accompanied by further chemical transformations that include dehydration, degradation, and condensation. As the temperature increase, the aromatic condensation reactions also take place among the adjacent molecules, which result in the evolution of gaseous products from the hydroaromatic structure of carbonized char leading to decrease yield of carbon [22].

Impregnation ratio is another critical parameter that affects the quality of the carbon. From Fig. 1 it is obvious that yield of carbon decrease as the impregnation ratio increase. Here the excess phosphoric acid will promote gasification of char and increased the total weight loss of carbon. The same result was also observed by other researchers [19,21,22].

3.2. *Characterizing pore structure of the carbons*

The structural heterogeneity of activated carbon plays an important role in adsorption processes, and numerous methods have consequently been developed and applied for the characterization of this property. In this study, we used nitrogen adsorption, scanning electron microscopy and X-ray diffraction methods to characterize our carbon samples.

3.2.1. *Nitrogen adsorption*

Identifying pore structure of adsorbents by the adsorption of inert gases is essential before liquid sorption experiments [23]. Fig. 2 illustrates adsorption/desorption isotherms of N_2 at −196 °C on activated carbons from jackfruit peel with different ratio of impregnation (IR) and different activation temperature.

Fig. 2(a) shows that the isotherms of samples prepared at 350 °C with different impregnation ratio are type III based on IUPAC classification, which arises from non-porous or macroporous surface. Here, the samples prepared at 350 °C practically do not contain micropores of different sizes in the entire porosity range studied and can be classified as non-porous materials. In type III isotherm, the interaction between carbon surfaces and adsorbate molecules are weak [24]. From Fig. 2(a) it can also be observed that the impregnation ratio gives no effect on the pore development.

Heat treatment temperature of 450 °C and impregnation ratio (IR) 1, gives type I isotherm (typical of microporous materials where micropore filling may take place by primary filling at very low relative pressure, p/p_o), but in this case a plateau is not clearly reached, indicating widening of pores; this isotherm exhibits a type H_4 hysteresis loop, characteristic of slit-shaped pores. As the impregnation ratio increase, the carbons posses combination of type I and type II isotherm, indicative of simultaneous presence of micro and mesopores. Baquero et al. [7] also observed similar evolutions from type I and type II

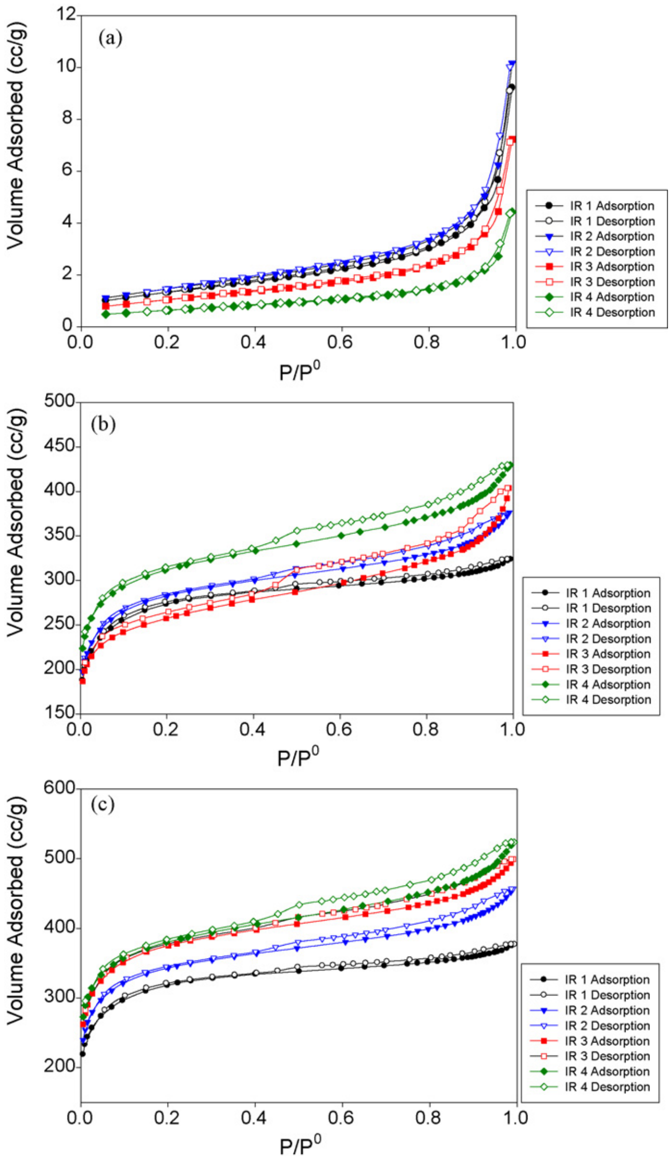

Fig. 2. N_2 adsorption isotherm for activated carbons at activation temperature 350 °C, (b) 450 °C, and (c) 550 °C.

Table 2
Characteristics of activated carbons prepared from jackfruit peel

Sample	S_{BET} (m^2/g)	V_{micro} (cm^3/g)	V_{meso} (cm^3/g)	V_{total} (cm^3/g)
IR[1]T[350]	4	–	–	–
IR[2]T[350]	5	–	–	–
IR[3]T[350]	4	–	–	–
IR[4]T[350]	2	–	–	–
IR[1]T[450]	907	0.401	0.124	0.525
IR[2]T[450]	937	0.428	0.135	0.563
IR[3]T[450]	956	0.431	0.147	0.578
IR[4]T[450]	1033	0.435	0.229	0.664
IR[1]T[550]	1056	0.454	0.159	0.603
IR[2]T[550]	1137	0.458	0.216	0.674
IR[3]T[550]	1090	0.449	0.178	0.627
IR[4]T[550]	1260	0.471	0.262	0.733

isotherms with increasing impregnation ratio. Similar results were also observed for activated carbon produced at 550 °C.

The effect of activation temperature and impregnation ratio on the BET surface area, micropore volume, and total pore volume are given in Table 2. The total pore volume, V_{total}, was calculated from nitrogen adsorption data as volume of liquid nitrogen at a relative pressure of 0.985. The micropore volume, V_{micro}, was determined by DFT method, and the mesopore volume, V_{meso}, was obtained by substraction of micropore volume and total pore volume.

The BET surface area and total pore volume increase with the increasing activation temperature. The increase in porosity with temperature can be attributed to the release of tars from cross-linked framework generated by the treatment of phosphoric acid [25]. At 450 °C, as the impregnation ratio is increased the micropore volume also increase, however the increase of micropore volume at impregnation ratio 2–4 is not significant and can be said approximately constant. On the other side, the mesopore volumes increase as the impregnation ratio raised. At higher temperature of activation (550 °C), the increase of micropore volume is not significant as seen in Table 2. In this temperature, the development of micropore already reached the maximum value and not affected by impregnation ratio. In general, the mesopore volume still increases with impregnation ratio. Mesopore development induced by phosphoric acid has also been reported by other studies [19,22,26]. However, one interesting phenomenon was observed on the pore structure of activated carbon obtained at impregnation ratio 3 and activation temperature of 550 °C. Here the pore structure parameters (BET surface area, micropore volume, mesopore volume) are lower than carbon obtained at impregnation ratio 2 and 4. This might be attributed to contraction of carbon structures and therefore, to reduction in porosity development.

The structural heterogeneity of porous material is generally characterized in terms of the pore size distribution. This pore size distribution represent a model of solid internal structure, which assumes that an equivalent set of non-interacting and regularly shaped model pores can represent the complex void spaces within the real solid [27]. The pore size distribution is closely related to both kinetic and equilibrium properties of porous material and perhaps is the most important aspect for characterizing the structural heterogeneity of porous materials used in industrial application. The pore size distribution of the samples was evaluated by density functional theory (DFT) method using medium regularization. The DFT pore size distribution of activated carbons studied is shown in Fig. 3.

This figure confirms that the activated carbons produced at carbonization temperature of 350 °C are non-porous materials, while the carbons obtained at 450 and 550 °C mainly micropores and some mesopores. For activated carbons produced at 450 °C, several strong peaks are observed for all impregnation ratio used in the study. The predominant pore width around 1.2, 1.5, and 1.9 nm, here the presence of ultramicropore (< 0.7 nm) is not observed. At 550 °C, the pore with size more than 2 nm (mesopore) being much more abundant and predominant pore width now shifts to 1.4 and 1.7. With the increase of temperature and impregnation ratio, the creation of micropore structure and widening of micropore to mesopore also occur.

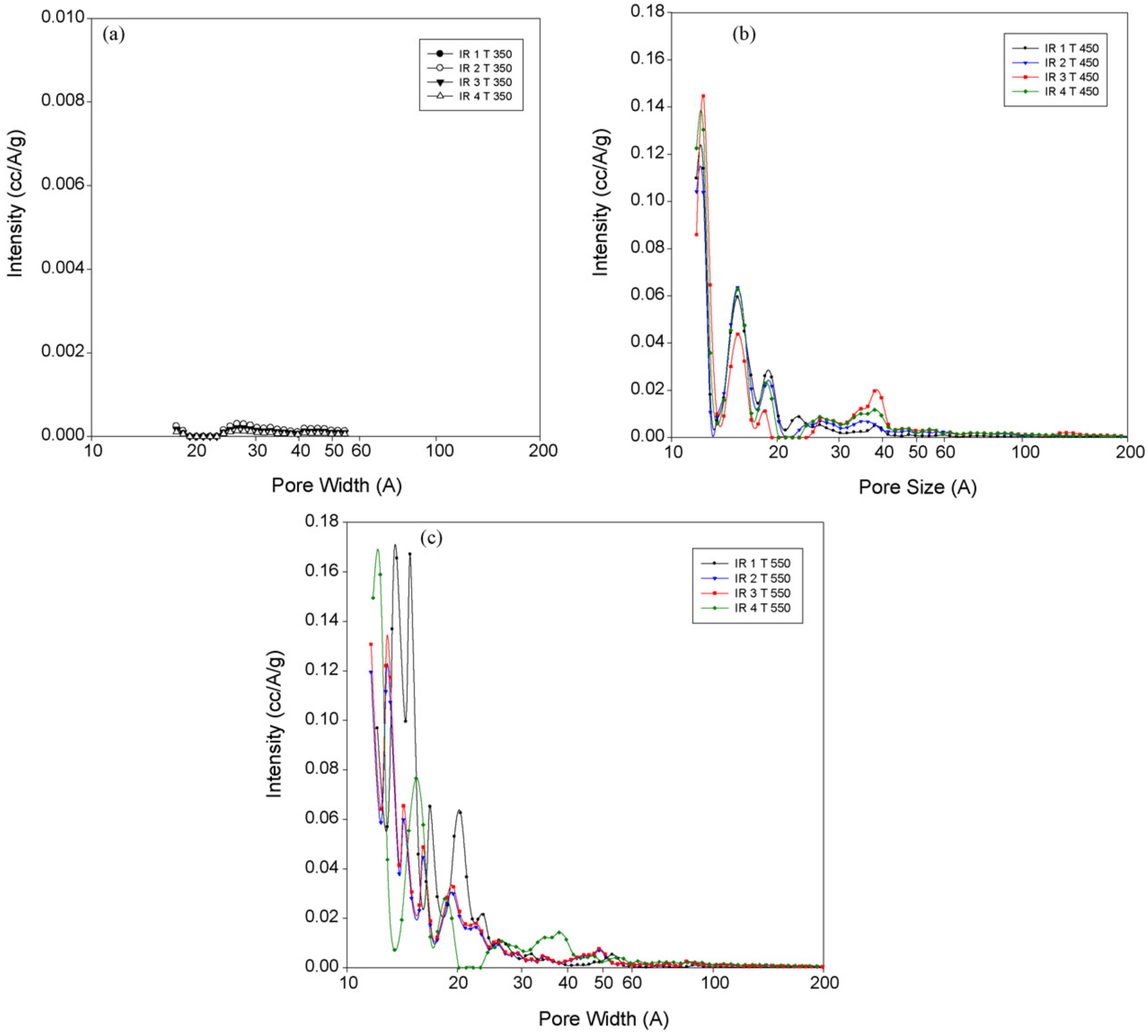

Fig. 3. DFT based pore size distribution of activated carbons produced at activation temperature (a) 350 °C, (b) 450 °C, and (c) 550 °C.

3.2.2. *Comparison of the external surfaces of resulting carbon using SEM*

Scanning electron micrographs of the surface morphology of several samples of the activated carbons are given in Fig. 4 This figure shows the differences of the external surfaces of the activated carbons prepared at R[4]T[350] and IR[4]T[450]. From this figures, it is obvious that the carbon produced at 350 °C are non-porous carbons, while the activated carbons produced at 450 °C has cavities on their external surface. It seems that the cavities on the surfaces of carbons resulted from the evaporation of the activating agent in this case is phosphoric acid during carbonization, leaving the space previously occupied by the activating agent.

3.2.3. *X-Ray diffraction*

Activated carbons produced from jackfruit peel using phosphoric acid activation can be crystallographically characterized by means of X-ray Diffraction. By XRD the interlayer spacing d_{002} is determined using the Bragg equation as follow:

$$d = \frac{\lambda}{2\sin\theta} \tag{1}$$

where λ is the X-ray wavelength and θ is the scattering angle for the peak position. The crystallite size along c-axis, L_c, and the size of the layer planes, L_a, are determined from the half-width of the diffraction peak using the Scherrer equation:

$$L = \frac{K\lambda}{B\cos\theta} \tag{2}$$

where L is L_c or L_a, B is the half-width of the peak in radians, and K is the shape factor. The quantities L_c and L_a are named stack height and stack width, respectively. The (0 0 2) and (1 0) peaks are used to calculate L_c and L_a, respectively. The shape factor K depends on the lattice dimension and the values $K = 0.9$ and $K = 1.84$ are used for calculation of L_c and L_a, respectively [24]. The XRD analysis was measured by Cu

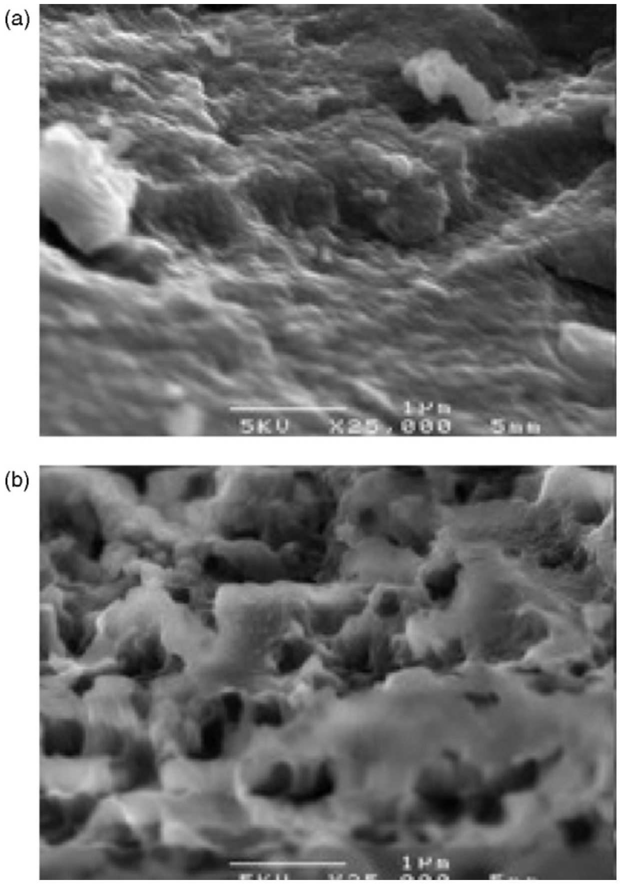

Fig. 4. SEM images carbons at (a) R[4]T[350], and (b)IR[4]T[450].

Kα with wavelength of 0.154 nm. The values of d_{002}, L_c, and L_a of activated carbons prepared from jackfruit peel are given in Table 3. The XRD curves are shown in Figs. 5–7.

The values obtained for interlayer spacing, d_{002}, remain practically unchanged with temperature and impregnation ratio. The d_{002} value, which is listed in Table 3, is in the range 0.35–0.36. These values are greater than that of graphite (0.335 nm). L_c for the carbons produced at 350 °C is slightly higher than that obtained at 450 °C and 550 °C, and have tendency to decrease with the activation temperature, and is of the order 1 nm. L_c and L_a values become slightly smaller as the surface area increase.

Table 3
Nanographitic structures and surface area of jackfruit peel activated carbon

Sample	d_{002} (nm)	L_c (nm)	L_a (nm)
IR[1]T[350]	0.36	1.25	1.66
IR[2]T[350]	0.36	1.25	1.59
IR[3]T[350]	0.36	1.30	1.63
IR[4]T[350]	0.36	1.30	1.59
IR[1]T[450]	0.36	1.25	1.34
IR[2]T[450]	0.36	1.21	1.29
IR[3]T[450]	0.36	1.16	1.29
IR[4]T[450]	0.36	1.08	1.25
IR[1]T[550]	0.35	1.25	1.59
IR[2]T[550]	0.35	1.16	1.46
IR[3]T[550]	0.35	1.09	1.35
IR[4]T[550]	0.35	1.02	1.30

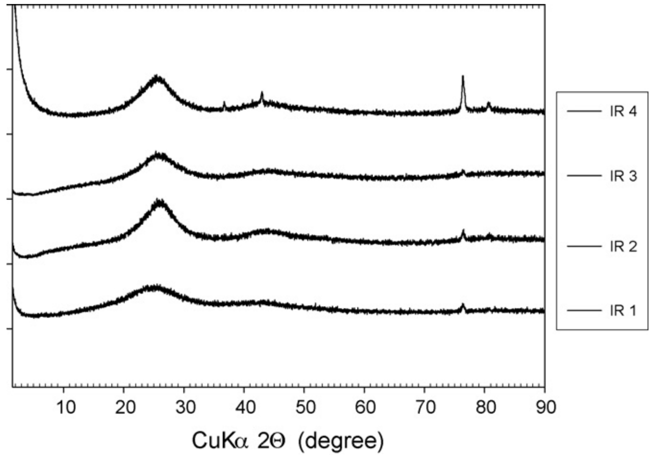

Fig. 5. XRD of activated carbons produced at activation temperature of 350 °C.

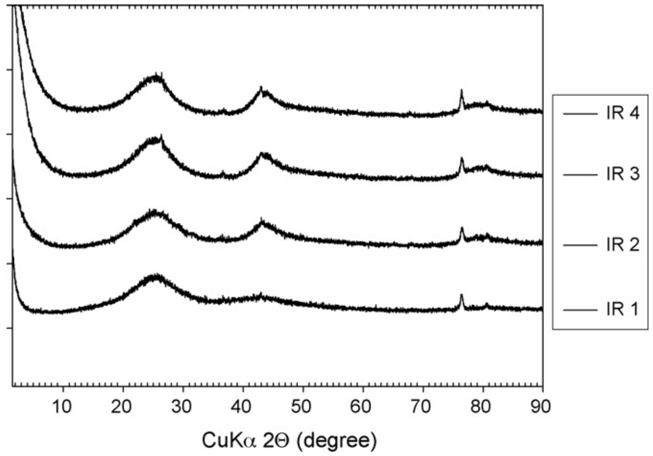

Fig. 6. XRD of activated carbons produced at activation temperature of 450 °C.

For these activated carbons, the diffraction profiles exhibited broad peaks at around 24 and 42° which are assigned to the reflection from (0 0 2) and (10) planes, respectively. The occurrence of broad peaks at these 2θ indicates an increasing regularity of crystal structure and resulting in better layer alignment [28].

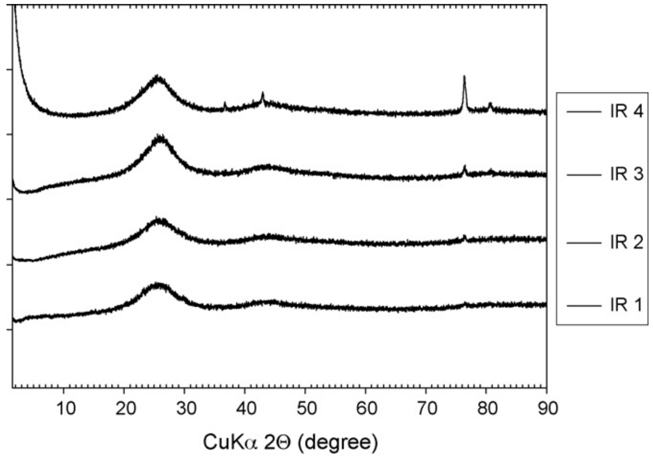

Fig. 7. XRD of activated carbons produced at activation temperature of 550 °C.

Table 4
Surface chemistry of jackfruit peel activated carbons

Sample	pH_{PZC}	Carboxylic (meq/g)	Lactonic (meq/g)	Phenolic (meq/g)	Acidic (meq/g)	Basic (meq/g)
IR[1]T[350]	1.9	1.3027	0.6525	0.8265	2.7816	0.0158
IR[2]T[350]	2.0	1.2592	0.6090	0.6960	2.5641	0.0808
IR[3]T[350]	1.9	1.3462	0.6090	1.0874	3.0426	0.0592
IR[4]T[350]	1.9	1.5202	0.8700	1.1744	3.5646	0.0375
IR[1]T[450]	1.9	1.0852	0.5655	0.7395	2.3901	0.0158
IR[2]T[450]	2.0	0.8242	0.3915	0.5655	1.7812	0.1025
IR[3]T[450]	1.9	0.8677	0.4785	0.5655	1.9117	0.0808
IR[4]T[450]	1.9	0.9112	0.7830	0.6090	2.3031	0.0592
IR[1]T[550]	2.0	0.7372	0.4350	0.3045	1.4767	0.0592
IR[2]T[550]	2.0	0.6067	0.3915	0.2610	1.2592	0.1242
IR[3]T[550]	2.0	0.7372	0.3915	0.2610	1.3897	0.1025
IR[4]T[550]	1.9	0.7807	0.7395	0.4350	1.9552	0.0808

3.3. Surface chemistry of the carbons

The carbon matrix does not consist of carbon atoms alone, but is also formed by other heteroatom like hydrogen, oxygen, nitrogen, halogen, sulfur, phosphorus, etc. These heteroatoms bonded to the edges of the carbon layers, which govern the surface chemistry of activated carbon. The surface chemistry of carbon materials is basically determined by the acidity and basicity of their surface. The existence of surface functional groups such as carboxyl, lactone, phenol, carboxylic anhydride, etc., has been postulated as constituting the source of surface acidity. Whereas the basic properties of activated carbon is associated with two types of structures: (i) the presence of oxygen containing groups, i.e. pyrone, chromene and carbonyl structures, at the edge of carbon crystallite; and (ii) oxygen free Lewis basic site on the graphene layers. The Lewis basicity of delocalized π electrons is influenced by the aromatic system on the carbon surface [16,29].

Table 4 shows quantitative surface chemistry analyses, which consist of amount of acidic and basic functional groups of jackfruit peel activated carbons. An example of point of zero charge (pH_{PZC}) determination of one of activated carbons, i.e. IR[1]T[550], is illustrated in Fig. 8. All of activated carbons show low pH_{PZC} in range of 1.9–2.0. These low pH_{PZC} values are consistent with Boehm titration result, which show dominance of acidic group at the surface of the activated carbons.

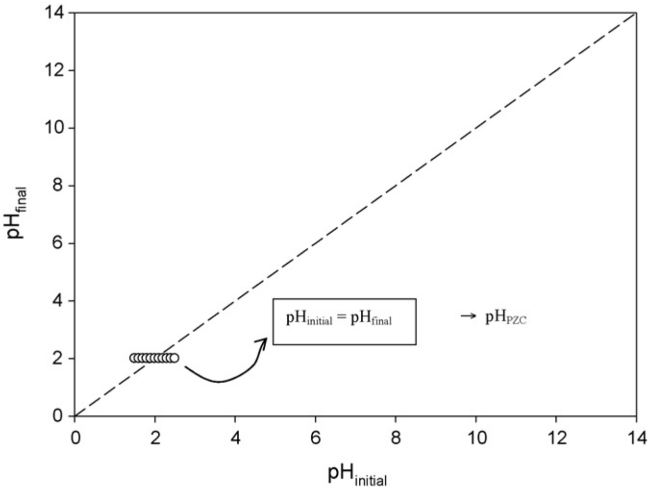

Fig. 8. pH_{PZC} Determination Using pH Drift Method of IR[1]T[550].

From Table 4, it can be seen that increasing activation temperature (at the same impregnation ratio) reduces the amount of acidic functional groups and increase the basic surface groups of the carbon. The increase of activation temperature will make several functional groups decompose to form CO and CO_2. This phenomenon is due to the instability of acidic groups at high temperatures [30]. On the other hand, basic groups are increased as the temperature is increased. These groups can be formed during cooling of the activated carbon after the heating process. This cooling process enables the fixation of oxygen in the active sites [30]. Similar result was also obtained by Guo and Rockstraw for phosphoric acid activated cellulose [17].

FTIR spectra of jackfruit peel activated carbons with various impregnation ratios at each activation temperature are illustrated in Fig. 9. All of spectra show broad absorption band around 3400–2400 cm^{-1}. A peak around 1710 cm^{-1} shows the presence of stretching vibration of C=O in ketones, aldehyde, lactone, and carboxyl. The presence of broadband around 3400–2400 cm^{-1} and peak around 1710 cm^{-1} indicates the presence of carboxylic acid [17,31].

A relative low intensity peak at wavenumber around 3100 cm^{-1} of the broadband around 3400–2400 cm^{-1} may also represent OH stretching vibration in phenol. Very weak peak around 2900 cm^{-1} is C–H stretching vibration in methyl group [31]. A strong band at 1590 cm^{-1} can be ascribed to C=C aromatic ring stretching vibration enhanced by polar functional groups [10]. There is also a presence of broadband between 1300 and 1000 cm^{-1} with the strong band around 1200 cm^{-1} and a shoulder around 1080 cm^{-1}. According to Puziy et al., the peak at 1220–1180 cm^{-1} may be ascribed to the stretching mode of hydrogen bonded P=O, O–C stretching vibrations in P–O–C linkage, and P=OOH; and the shoulder at 1080–1070 cm^{-1} can be ascribed to ionized linkage $P^+–O^-$ in acid phosphate esters and to symmetrical vibration in a chain of P–O–P.

FTIR spectra for the raw material and the activated carbons with different activation temperature are given in Fig. 10.

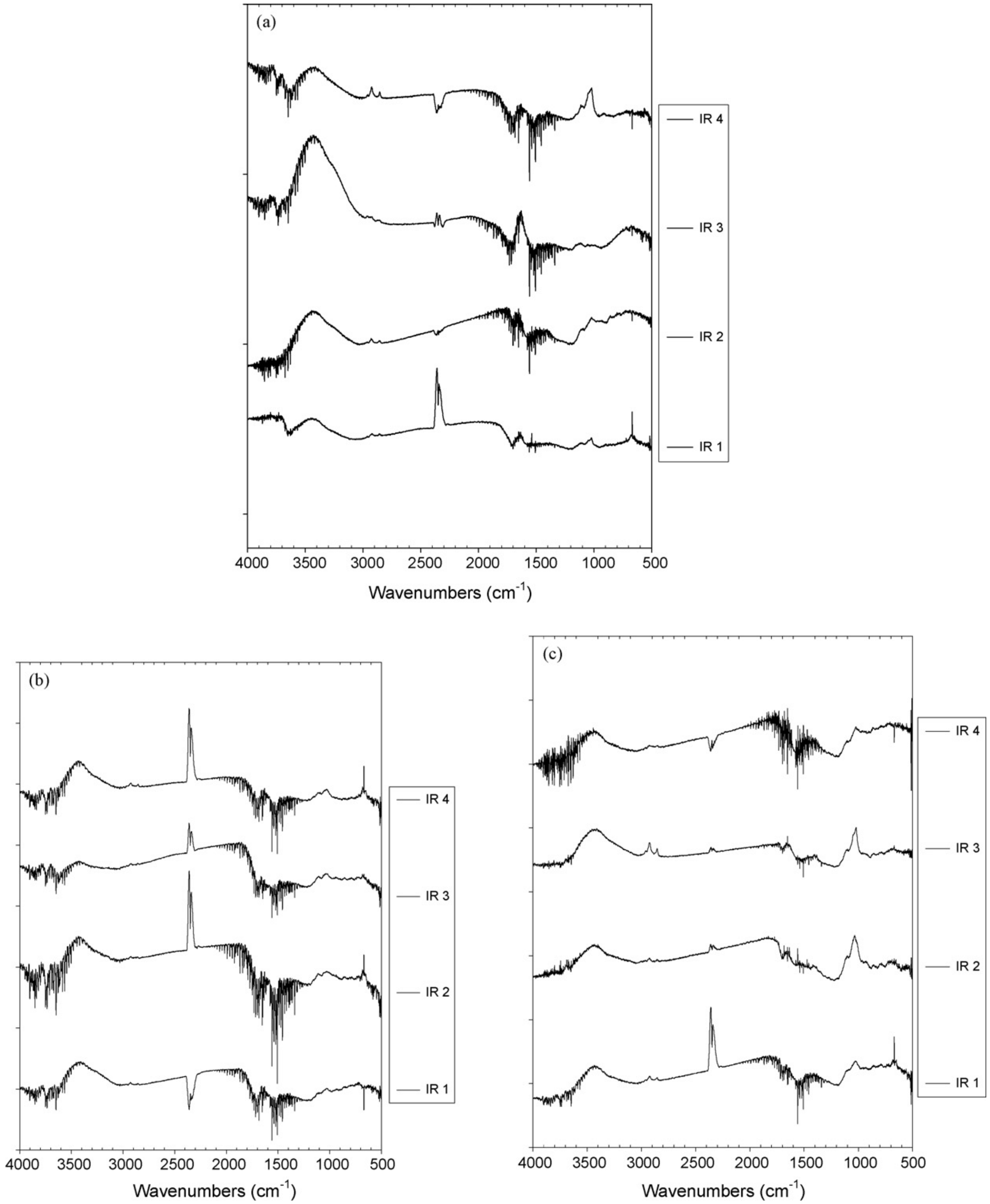

Fig. 9. Fourier Transform Infra Red Spectra for Jackfruit Peel Activated Carbon at activation temperature (a) 350, (b) 450, and (c) 550 °C.

There are significant changes of the absorption band from raw material compared with activated carbon product. Band around 3600–3200 cm^{-1} which can be attributed to hydroxyl group or adsorbed water and band around 1100 cm^{-1} seems to disappear by the carbonization at certain activation temperature, i.e. 350, 450, 550 °C, of raw material to activated carbon. As the activation temperature increases from 350 to 550 °C, the relative intensity for the peak around 1710 cm^{-1} decrease. This behavior agrees with Boehm titration result which also shows decreasing tendency of carboxylic acid group as activation temperature increases. Phosphorous containing group seems to be more obvious as activation temperature increases from 350 to 550 °C. At 550 °C, the phosphorous functional group around 1200 cm^{-1} becomes dominant.

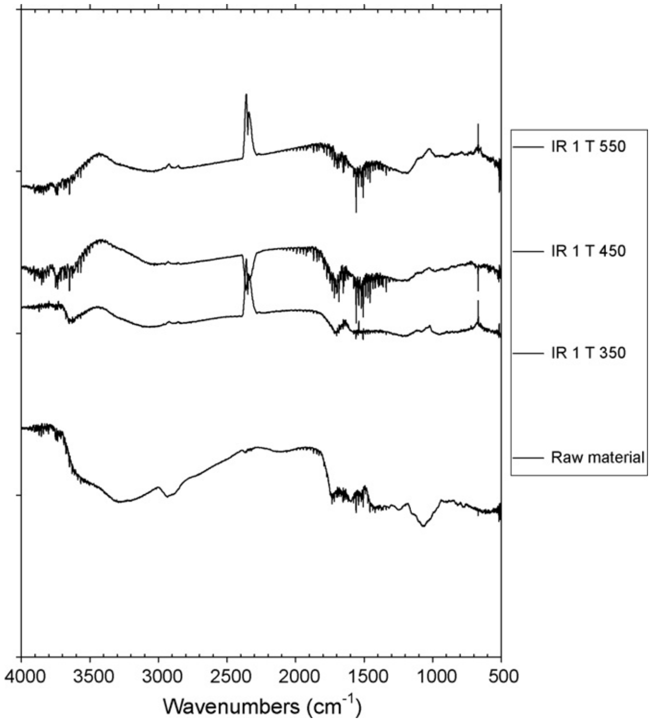

Fig. 10. Comparison of FTIR of Jackfruit Peel Activated Carbon with Impregnation Ratio 1 and activation temperature of 350, 450, and 550 °C and The Raw Material.

4. Conclusion

Activated carbons were prepared from jackfruit peel using phosphoric acid as chemical activating agent. The effect of impregnation ratio and activation temperature on pore structure and surface chemistry of resulting carbons were also studied. The pore structure of the carbons was studied by nitrogen adsorption, XRD dan SEM, and its surface chemistry was determined by Boehm titration method and FTIR. Non-porous carbons were produced at activation temperature of 350 °C, and carbons with well-developed pores are produced at activation temperature of 450 and 550 °C. By increasing activation temperature (at the same impregnation ratio) the amount of acidic functional groups decreases while the basic surface groups of the carbon are increase.

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