

# Preparation and Characterization of Activated Carbon from Apple Waste by Microwave-Assisted Phosphoric Acid Activation: Application in Methylene Blue Adsorption

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Activated carbons (ACs) prepared from *apple pulp* and *apple peel* with phosphoric acid as an activation agent under microwave radiation were investigated. The effects of microwave radiation power and time on the adsorption capacities of the ACs were studied. The optimum AC preparation condition was identified by comparing the MB adsorption capacities of the produced ACs. The obtained results show that the microwave radiation power and time had strong effects on the adsorption capacities. Relative to conventional heating methods, microwave-prepared ACs showed higher BET surface areas and mesopore volumes after a shorter activation time due to differences in the type of heat transfer between these two methods. The N<sub>2</sub> adsorption isotherms at -196°C and SEM and FTIR results were used to characterize the properties of the prepared ACs. The N<sub>2</sub> adsorption results revealed BET surface areas of 1552 m<sup>2</sup>/g and 1103 m<sup>2</sup>/g for apple-peel and apple-pulp-based AC, respectively.

*Keywords:* Activated Carbon; Microwave; Chemical activation; Adsorption; Pore structure

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## INTRODUCTION

Activated carbon (AC) has recently been used as an adsorbent due to its capacity for adsorption from the gas and liquid phases (Daifullah *et al.* 2003). ACs are used in wastewater treatment, drinking water purification (Heijman and Hopman 1999), and liquid-phase adsorption. ACs are also used for gas phase adsorption in air pollution control (Tsai *et al.* 1998). The high applicability of AC is related to its high porosity, rapid adsorption, and thermal stability (Hesas *et al.* 2013).

Producing inexpensive AC is one of the main challenges in commercial manufacturing. To this end, new production techniques and the use of inexpensive raw materials have been studied (Budinova *et al.* 2006), including the use of agricultural waste as an inexpensive precursor with high carbon content and low inorganic content (Arami-Niya *et al.* 2011 & 2012). Apple waste is the solid residue generated in juice and cider manufacturing, over 0.8 million metric tons of which is generated each year worldwide (Suárez-García *et al.* 2001). Apple waste was used in this study as an AC precursor for chemical activation (Suárez-García *et al.* 2002).

Conventional heating is one of the most applicable preparation methods for producing AC. In this method, heat is transferred to the samples by conduction, convection, and radiation mechanisms. The surface of the particles is heated before their interiors, inducing a thermal gradient between the surface and core of each particle (Thostenson and Chou 1999; Yadoji *et al.* 2003). This thermal gradient leads an inhomogeneous microstructure for high heating rates (Oghbaei and Mirzaee 2010). As an alternative heating method, microwave irradiation has produced promising results over the last several years in the production of low-cost and homogeneous AC with high energy savings. These results are related to the direct heating of the particle interior by microwave heating, which induces rapid volumetric heating (Thakur *et al.* 2007; Xie *et al.* 1999).

Biological, chemical, and physical methods are three categories of dye removal technologies which have not been applied widely at large scale due to the high cost and disposal problems (Ghoreishi and Haghghi 2003). Various physical techniques have been employed for the removal of dyes from wastewaters includes membrane filtration, chemical precipitation, carbon adsorption, co-precipitation/adsorption, and ion exchange (Ferrero 2007). Among the physical technologies, adsorption has been proved to be an excellent way to treat industrial waste effluents due to the significant advantages such as low cost, availability, profitability and efficiency especially from economical and environmental points of view (Banat *et al.* 2003).

Methylene Blue (MB) is a heterocyclic aromatic chemical component (Hirata *et al.* 2002) which was most commonly used by the cotton, wool, and silk dyeing industries. Acute exposure to MB can cause harmful effects in humans such as increase in heart rate, vomiting, shock, Heinz body formation, cyanosis, jaundice, quadriplegia, and tissue necrosis (Vadivelan and Kumar 2005). Therefore, MB removal from waste streams of these industries has been one of the important applications of adsorption from the aqueous phase (Ioannidou and Zabaniotou 2007)

*Apple pulp* was used to produce AC using the conventional heating method of Suárez-García *et al.* (2002a), which uses chemical activation with phosphoric acid as a chemical agent. Jagtoyen and Derbyshire (1998) found that phosphoric acid catalyzes the reactions of acid dehydration, promotes depolymerisation reactions of the lignocellulosic matter, and facilitates the loss of hydrogen, favouring enrichment in carbon. The activation of biomass by phosphoric acid occurs through various steps and includes: cellulose depolymerization, biopolymers dehydration, formation of aromatic rings, and elimination of phosphate groups (Benaddi *et al.* 1998).

The objective of this study was to prepare AC from apple waste using  $H_3PO_4$  chemical activation with microwave radiation to identify the effects of certain procedural variables and to compare the properties of the produced AC with those produced by the conventional heating method. To the best of our knowledge, no study has been performed on the production and characterization of apple-waste-based AC using microwave heating.

Therefore, this study aimed to evaluate the effects of microwave radiation time and power on the yield and adsorption capacity of AC produced from apple waste in the form of *apple pulp* and peel. The products were characterized in terms of adsorption of methylene blue (MB) and several laboratory analyses (TGA, CHN/O, SEM, and surface area analysis) to determine their chemical and physical properties.

## MATERIALS AND METHODS

### Materials

Methylene blue, an odorless dark-green solid at room temperature with a chemical formula of  $C_{16}H_{18}N_3$  and molecular weight of 319.85 g, was purchased from Merck (M) Sdn. Bhd, Malaysia. Phosphoric acid 85% was purchased from Merck (M) Sdn, Bhd. Deionized water supplied by the USF ELGA water treatment system was used to prepare all reagents and solutions. Apples were bought from a local market; the *apple peel* was removed, and the remaining solid residue was used as pulp (*apple pulp*). The proximate and elemental analysis results for the dried raw materials are shown in Table 1.

**Table 1.** Proximate and Elemental Analysis of Raw Materials and Prepared ACs

Material	Moisture (%)	Volatile (%)	Ash (%)	Fixed Carbon (%)	C (%)	H (%)	N (%)	O (%)
Dried pulp	6.00	92.03	0.88	1.078	42.74	6.69	0.90	49.66
Dried peel	10.72	87.40	0.50	1.37	43.63	7.43	0.63	48.30
Pulp AC	15.11	62.96	15.35	6.56	74.30	2.77	1.55	21.37
Peel AC	12.27	72.89	7.43	7.40	72.52	2.75	0.97	23.75

### Preparation of Activated Carbons

The *apple peel* was separated, and the remaining part of the apple was pressed to separate the cider. The moist solid residue and removed *apple peel* were spread on a metal tray and dried for 15 days at ambient temperature and 6 days at 35 °C. The mass loss of the pulp and peel after drying were 88.70% and 86%, respectively. The dried samples were ground using a knife mill and passed through a 1 mm sieve for homogenization. The incipient wetness method by drop-wise addition is regarded as the best variant of the incipient wetness methods (Suárez-García *et al.* 2002b). To facilitate the homogeneous absorption of the liquid, the solid particles should be stirred in the solution. The necessary amount of acid for pulp was determined to be 3.5 mL per gram of solid to increase swelling during incipient wetness. However, this amount of phosphoric acid was not sufficient to induce good swelling of the peel. The minimum amount of  $H_3PO_4$  necessary to produce a homogeneous peel solution was 4.5 mL per gram of peel. The impregnation ratio, defined as the gram of  $H_3PO_4$  impregnated per gram of precursor, was 1.5 (g  $H_3PO_4$ /g precursor).

Approximately 6 g of each precursor was impregnated with phosphoric acid (85% wt) at an impregnation ratio of 1.5 and placed in an oven to dry for 4 h at 110 °C. The dried and impregnated samples were placed on a quartz tray and inserted into a 2.45 GHz modified microwave oven (Panasonic (NN-CD997SMPQ)) with different powers (550, 700, and 1000 W) and radiation times of 10, 12.5, and 15 min for pulp and 5, 7.5, and 10 min for peel.

Nitrogen gas at a pre-set flow rate of 300 cm<sup>3</sup>/min was used to purge the air inside the microwave before and during the activation process. The obtained samples were cooled to room temperature and then washed several times with distilled water to the pH 6-7 (measured with a Mettler Toledo pH/conductivity meter, model MPC227). Next, the resulting ACs were dried for 12 h at 110 °C in a vacuum furnace. The different activation conditions are listed in Table 2.

**Table 2.** Prepared Samples in Different Conditions

Pulp	MW Power (W)	MW Radiation Time (min)	MB adsorption (%)	Peel	MW Power (W)	MW Radiation Time (min)	MB adsorption (%)
1	550	10	49.69	10	550	5	68.36
2	700	10	80.23	11	700	5	69.4
3	1000	10	83.78	12	1000	5	70.12
4	550	12.5	53.27	13	550	7.5	70.1
5	700	12.5	94.6	14	700	7.5	82.2
6	1000	12.5	83.83	15	1000	7.5	80.24
7	550	15	60.71	16	550	10	71.02
8	700	15	88.27	17	700	10	92.96
9	1000	15	83.95	18	1000	10	80.25

### Characterization Techniques

The proximate analysis of both precursors was conducted according to ASTM D 7582-10, and the results are expressed in terms of moisture, volatile matter, fixed carbon, and ash contents. The carbon, hydrogen, nitrogen, and oxygen content of the samples were measured using a CHNS/O analyzer (model 2400 Perkin-Elmer, Series II).

A Micromeritics ASAP-2020 instrument was used for the adsorption isotherms of N<sub>2</sub> at -196 °C to clarify textural properties of produced ACs. Prior to measurement, the samples were degassed under vacuum at 350 °C and 10<sup>-5</sup> Torr for 10 h. Approximately 0.15 g of the degassed samples was used in each adsorption experiment. By analyzing the N<sub>2</sub> adsorption profile, the BET surface area, micropore volume, total pore volume, and pore size distribution were obtained. The BET method was used to determine the specific surface area at relative pressures in the range of 0.05 to 0.30 (Sing 1998). The held volume of nitrogen at the highest relative pressure (0.99) was used directly to estimate the total pore volume. The Dubnin-Radushkevich (DR) equation was used to estimate the micropore volume (Barrett *et al.* 1951; Rouquerol *et al.* 1999).

Scanning electron microscopy (SEM) was used to identify the surface physical morphology. A JSM-6390LV (JEOL Ltd., Japan) instrument with a 3 kV accelerating voltage was used to characterize the morphology of ACs, which were dried overnight at approximately 105 °C under vacuum before SEM analysis.

The chemical functionality of peel- and pulp-based ACs was qualitatively identified by Fourier transform infrared spectroscopy (FTIR). FTIR spectra were recorded between 4000 and 400 cm<sup>-1</sup> using an AVATAR 360 spectrophotometer (Thermo Nicolet Co., USA). The transmission spectra of the samples were recorded using KBr pellets (0.1% sample).

MB (basic), with C.I. Classification Number of 52,015, a chemical formula of C<sub>16</sub>H<sub>18</sub>N<sub>3</sub>ClS, MW= 319.85, and λ max = 668 nm (Foo and Hameed 2012), is a dark green powder. This analytical grade cationic dye was chosen in this study to measure adsorptive properties of the produced ACs. The adsorptive properties of the produced ACs were measured using MB as an adsorbate. MB is adsorbed on the acidic sites of the ACs (Hirata *et al.* 2002; Wartelle *et al.* 2000) and accessible to pores with diameters larger than 1.5 nm (Deng *et al.* 2010a). The adsorption capacity of MB was listed as a specification parameter for commercial ACs. Thus, we selected MB as the response to determine the optimum preparation conditions. The MB number (q<sub>MB</sub>, mg/g carbon) of AC was measured according to the standard accepted methods (Deng *et al.* 2009).

A 100 mL volume of 300 mg/L MB solution was placed in an Erlenmeyer flask (250 mL) for the adsorption test. The prepared AC (0.1 g, particle size of <250  $\mu\text{m}$  that were obtained by grinding and sieving of AC samples) was added to each flask, and the flasks were then shaken in an isothermal shaker at 120 rpm at 30 °C for 24 h to reach equilibrium. Prior to the analysis, all samples were filtered to prevent interference from carbon fines. A double-beam UV–visible spectrophotometer (Perkin Elmer) at 664 nm was used to measure the MB concentration. The amount of MB adsorbed per unit mass of adsorbent at equilibrium conditions,  $q_e$  (mg/g), was calculated by (Daneshvar *et al.*, 2002),

$$q_e = (C_0 - C_t) * V/m \quad (1)$$

where  $C_0$  ( $\text{mg L}^{-1}$ ) is the initial concentration of MB,  $C_t$  ( $\text{mg L}^{-1}$ ) is the residual MB concentration in solution at time  $t$ ,  $V(L)$  is the volume of the solution, and  $m$  (g) is the mass of AC. The measurement of each sample was replicated twice and averaged. To calculate the MB adsorption efficiency by prepared ACs, the following equation was used:

$$\text{Adsorption}(\%) = \frac{C_0 - C_t}{C_0} \times 100 \quad (2)$$

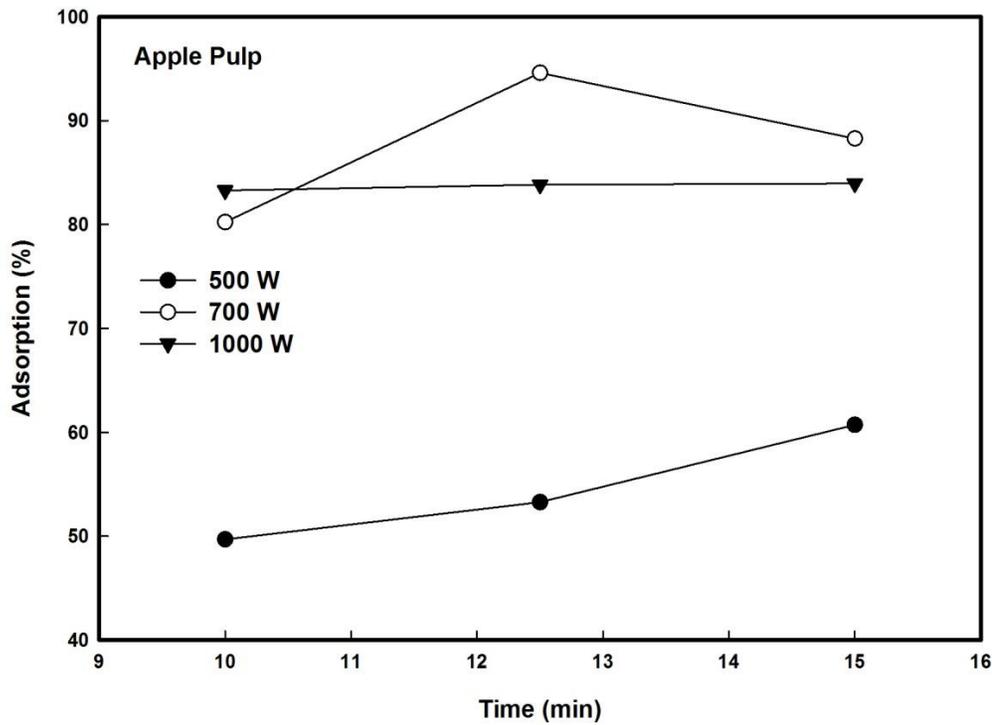
## RESULTS AND DISCUSSION

### Effects of Radiation Time on Activated Carbon Adsorption Capacity

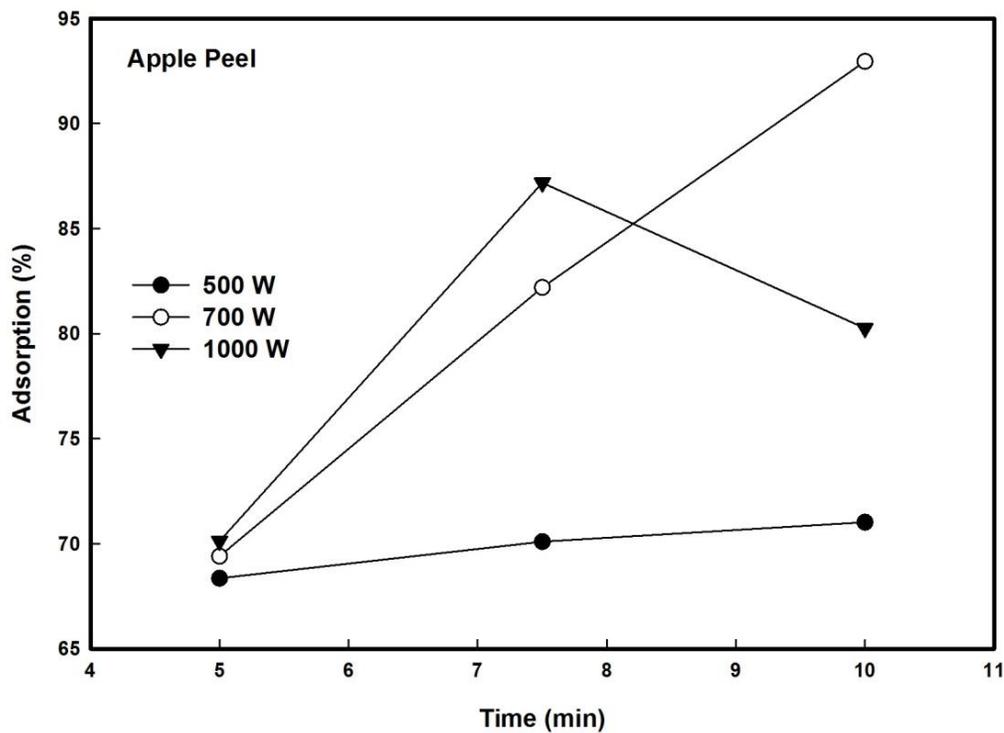
The effects of microwave radiation time on the adsorption capacity of the pulp- and peel-based ACs are shown in Figs. 1 and 2, respectively. The adsorption was evaluated at microwave powers of 550, 700, and 1000 W for radiation times of 10, 12.5, and 15 min for pulp and 5, 7.5, and 10 min for peel at an impregnation ratio of 1.5 (g  $\text{H}_3\text{PO}_4/\text{g}$  precursor).

For the pulp (Fig. 1), the adsorption increased by approximately 20% when the activation time was increased from 10 to 15 min at low microwave power (550 W), indicating the formation of a greater number of active sites and pores inside and on the surface of the samples. At 700 W, the adsorption increased with the activation time from 10 to 12.5 min and then decreased from 12.5 to 15 min. In this case, the created pores may be burnt off and reformed beginning at 12.5 min, causing the release of adsorbed MB with increasing radiation time. Similar trends were also found by Deng *et al.* (2009), and Li *et al.* (2008).

The adsorption was approximately constant with increasing activation time at 1000 W, which may be due to the agglomeration of the micropores and mesopores into larger pores at high microwave powers. The maximum adsorption likely occurred at an activation time of less than 10 min. This phenomenon was observed by Deng *et al.* for AC prepared from cotton stalk using microwave radiation (Deng *et al.* 2010a). According to these results, highest adsorption, 94.6% (283.8 mg/g), was achieved under activation conditions of 700 W and 12.5 min for pulp-based AC.



**Fig. 1.** Effect of activation time on MB adsorption of the produced pulp-based ACs at different MW powers (500, 700, and 1000 W)

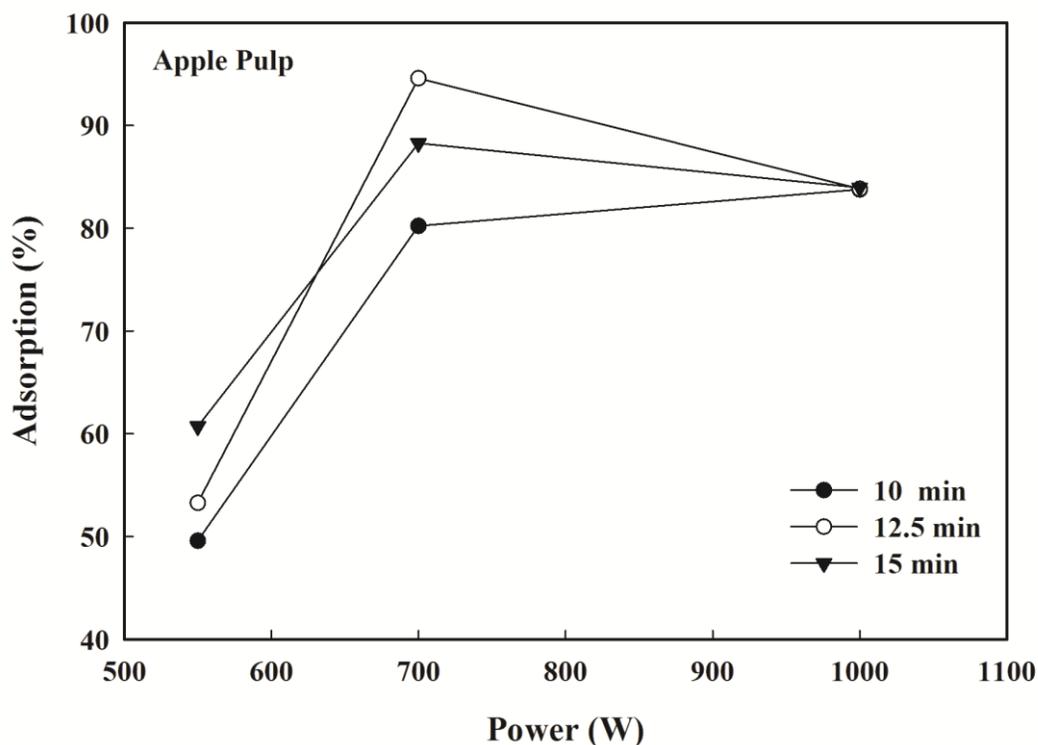


**Fig. 2.** Effect of activation time on MB adsorption of the produced peel-based ACs at different MW powers (500, 700, and 1000 W)

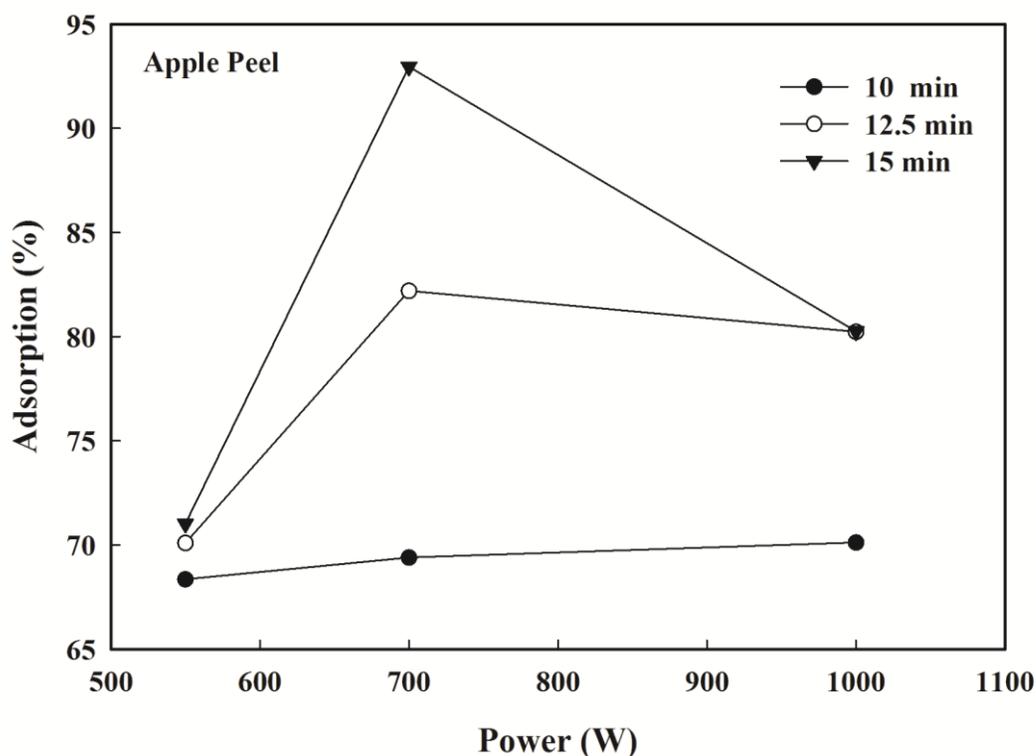
In the case of peel (Fig. 2), the adsorption rate for 550 W had the same tendency as that for pulp at the same power, with a higher adsorption rate under the same activation conditions. At 700 W, the MB adsorption increased with activation time due to the better activation achieved by opening previously inaccessible pores and the formation of new pores (Foo and Hameed 2011). At 1000 W, the adsorption decreased as the microwave radiation time increased from 5 to 7.5 min and then decreased as the radiation time was increased to 10 min for the same reason mentioned for pulp-based AC at 700 W and 12.5 min. The highest adsorption (87.18%) at 1000 W was observed at around 7.5 min of treatment, after which it decreased.

### Effects of Radiation Power on Activated Carbon Adsorption Capacity

Heating the carbon precursors without chemical impregnation is very difficult, and the activation agents act as the primary microwave absorber at the beginning of radiation in the activation stage. With the further development of pore structure, the AC itself can absorb microwave energy (Wang *et al.* 2009). Figures 3 and 4 show the effect of microwave power on the adsorption performance of the pulp- and peel-based AC, respectively. The adsorption of pulp-based AC (Fig. 3) increased significantly from 49.60 to 80.23% when the power was increased from 550 to 700 W at a constant radiation time of 10 min. High microwave power improves the development of the pore structure of AC, which indicates that microwave power is important in the activation stage. However, the equilibrium adsorption of MB did not change significantly when the power was increased to 1000 W due to a decrease in the formation rate of new pores and beginning of pore destruction.



**Fig. 3.** Effect of MW power on MB adsorption of the produced pulp-based ACs at different activation times (10, 12.5, and 15 min)



**Fig. 4.** Effect of MW power on MB adsorption of the produced peel-based ACs at different activation times (10, 12.5, and 15 min)

At a constant radiation time of 12.5 min, the adsorption percentage increased from 53.27% to 94.60% when the activation power was increased from 550 W to 700 W and then decreased to 83.83% when the microwave power was increased to 1000 W. Excessive microwave energy could burn the carbon, destroying the pore structure and thereby reducing the adsorption (Foo and Hameed 2012). The trends in adsorption with radiation power after 15 min of irradiation have the same cause as those after 12.5 min of irradiation. Importantly, the optimum adsorption occurred at a microwave power between 550 W and 700 W for 15 min of activation. Thus, the amount of adsorption at 700 W (88.27%) is that obtained amount during pore structure destruction by high microwave radiation.

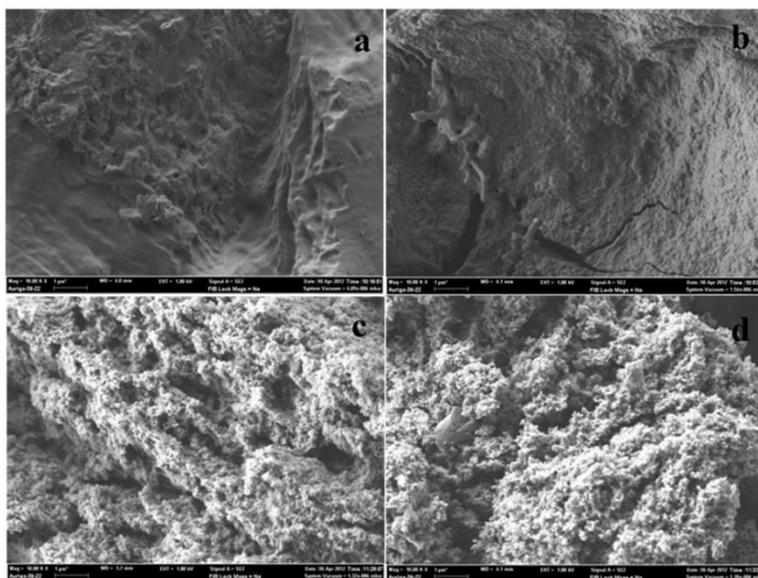
In the case of peel-based AC, Fig. 4 shows the effect of microwave power on the adsorption capacity of the produced ACs. At constant radiation times of 7.5 min and 10 min, the adsorption capacity increased and then decreased with increasing radiation power due to burning of the carbon and destruction of the pore structure by excess microwave energy.

The highest MB adsorption (92.96% or 277.8 mg/g) was achieved at a microwave power of 700 W and radiation time of 10 min for the peel-based AC. Deng *et al.* (2010) prepared cotton stalk-based AC by microwave assisted phosphoric acid chemical activation, where they achieved maximum MB adsorption of 245.70 (mg/g). The maximum MB adsorption of 200.00 (mg/g) was obtained by Wang *et al.* (2009), where they used cotton stalk to prepare AC by using microwave method with zinc chloride chemical activation.

## Characterization of Activated Carbon

### *Surface morphology of activated carbon*

Scanning electron microscopy (SEM) was used to observe the surface physical morphology of the samples. Figure 5 shows the SEM images of the microstructures of the raw pulp and peel and the derived ACs. The surfaces of the raw materials (Fig. 5a and 5b) were fairly smooth, with few cracks or voids. The SEM images of the pulp-based AC (Fig. 5c) and peel-based AC (Fig. 5d) show that the activation stage produced extensive external surfaces with quite irregular cavities and pores. The surface topology differed strongly between raw materials and prepared ACs. High porosity was observed on the external surface of the ACs. These pores result from the evaporation of the chemical reagent ( $H_3PO_4$ ) during carbonization, leaving empty spaces (Deng *et al.* 2010b). In contrast, as observed from Fig. 5c and d, small, narrow pores were observed on the surface of the peel and pulp-based ACs but not the raw materials. These pores can be attributed to the lower propensity for pore coarsening due to the shorter sintering time in the microwave method (Oghbaei and Mirzaee, 2010).



**Fig. 5.** SEM micrographs (10000X) of the a.) pulp, b.) peel, c.) pulp-based AC, and d.) peel-based AC

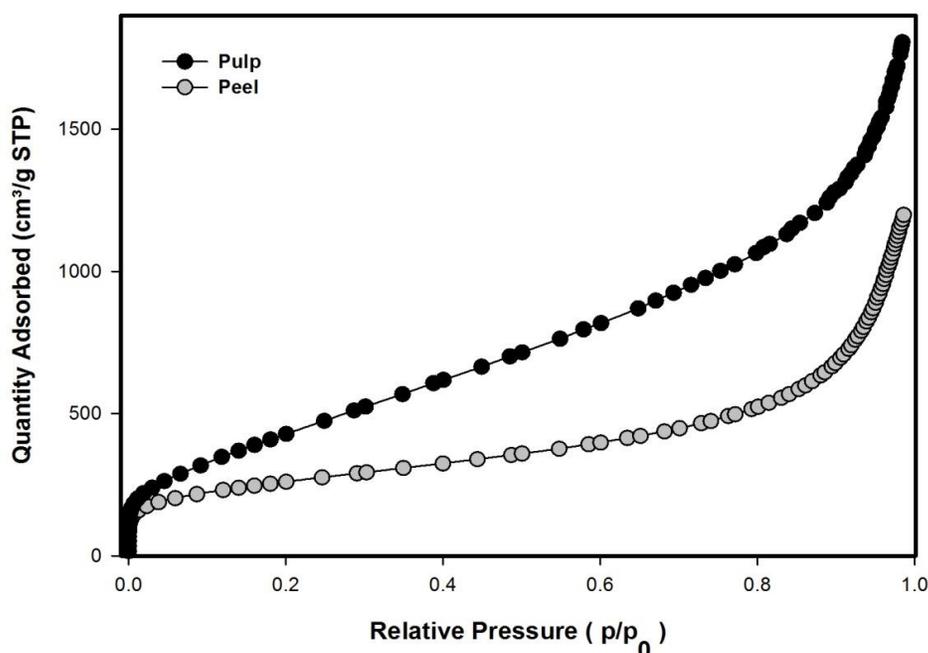
### *Specific surface area and pore structure of the activated carbon*

Nitrogen isotherms at  $-196^{\circ}C$  were used to compare the specific surface area and pore structure of the samples with maximum MB adsorption. The nitrogen isotherm adsorption of pulp-based AC (700 W, 12.5 min) and peel-based AC (700 W, 10 min) are shown in Fig. 6. According to the IUPAC classification, both isotherms were of type II, indicating unrestricted monolayer-multilayer adsorption. The filling of the micropores with nitrogen molecules occurs in the initial part of the type II isotherm, whereas the slope of the plateau at high relative pressure represents multilayer adsorption *via* mesopores, macropores, and the external surface (Rouquerol *et al.* 1999). The changes in the slope of both isotherms at point  $P/P_0 > 0.1$  indicate that the monolayer coverage stage is completed and that multilayer adsorption is about to begin (Zhang *et al.* 2009). As

shown in Fig. 6, the  $N_2$  isotherm of peel-based AC exhibited a greater slope than that of pulp-based AC, which indicates higher multilayer adsorption by peel-based AC.

The reactivity and combustion behavior of the AC is strongly affected by  $S_{BET}$  (Pütün *et al.* 2005). Further, the adsorption capacity of AC is mainly related to the  $S_{BET}$ , pore size distributions, and pore volume (El-Hendawy *et al.* 2001). By using the microwave heating method, a higher  $S_{BET}$  value can be obtained compared with that reached using conventional heating method in an initial short stage due to the different heating mechanisms used in these two methods.

The BET surface area ( $S_{BET}$ ), total pore volume ( $V_t$ ), micropore pore volume ( $V_{mic}$ ), and average pore diameter ( $D_p$ ) of pulp and peel-based ACs prepared by microwave method and pulp-based AC prepared by conventional method (Suárez-García *et al.* 2002) are listed in Table 3. The values of  $S_{BET}$  in Table 3 are for the ACs with higher MB adsorption capacity. The BET surface area ( $S_{BET}$ ), total pore volume ( $V_t$ ), micropore pore volume ( $V_{mic}$ ), and average pore diameter ( $D_p$ ) obtained by applying the BET equation to  $N_2$  adsorption at  $-196^\circ\text{C}$  are listed in Table 3. The mesopore pore volume ( $V_{meso}$ ) in Table 3 was calculated by subtracting the micropore volume from the total pore volume.



**Fig. 6.** Volume of  $N_2$  adsorption isotherm versus relative pressure for pulp-based AC (700 W, 12.5 min) and peel-based AC (700W, 10 min)

**Table 3.** Porous Structure Parameters of Activated Carbon

Properties	MW <sup>(a)</sup> - Pulp based AC	MW- Peel based AC	C <sup>(b)</sup> - Pulp based AC
$S_{BET}$ (m <sup>2</sup> /g)	1103	1552	854
$V_t$ (cm <sup>3</sup> /g)	1.76	2.59	0.45
$V_{mic}$ (cm <sup>3</sup> /g)	0.47	0.88	0.32
$V_{meso}$ (cm <sup>3</sup> /g)	1.29	1.71	0.13
$D_p$ (nm)	7.81	6.68	-

(a) Microwave activated carbon; (b) Conventionally activated carbon

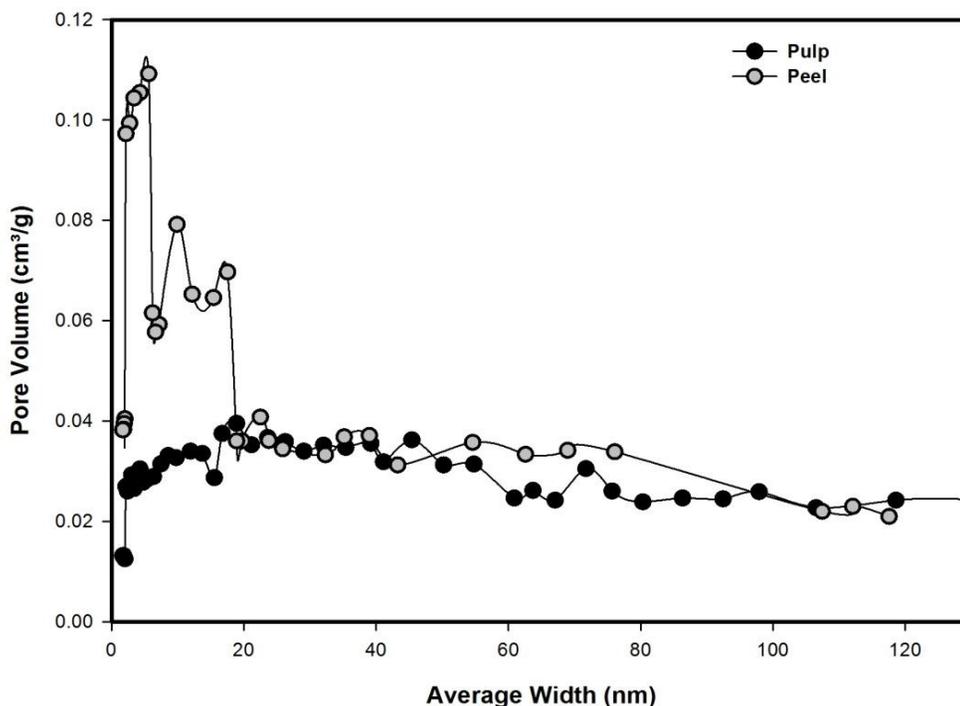


Fig. 7. Pore size distribution of pulp- and peel-based ACs

The BET surface area mentioned in Table 3 may not be the highest achievable surface area, as these  $S_{BET}$  values are for the ACs with the highest MB adsorption capacity. Other prepared ACs with lower adsorption capacity could have a greater number of micropores and an effectively higher BET surface area. Although, peel-based AC has a higher BET surface area, its MB adsorption is almost identical to that of pulp-based AC. The high degree of similarity for the MB adsorption of pulp- and peel-based ACs despite their differing BET surface areas could be related to the pore size required for MB adsorption. Because MB is mostly adsorbed in mesopores, the large micropore volume of peel-based AC ( $0.88 \text{ cm}^3/\text{g}$ ) compared to pulp-based AC ( $0.47 \text{ cm}^3/\text{g}$ ) does not play a significant role in the monolayer adsorption of MB in comparison with multilayer adsorption at mesopores, macropores, and the external surface.

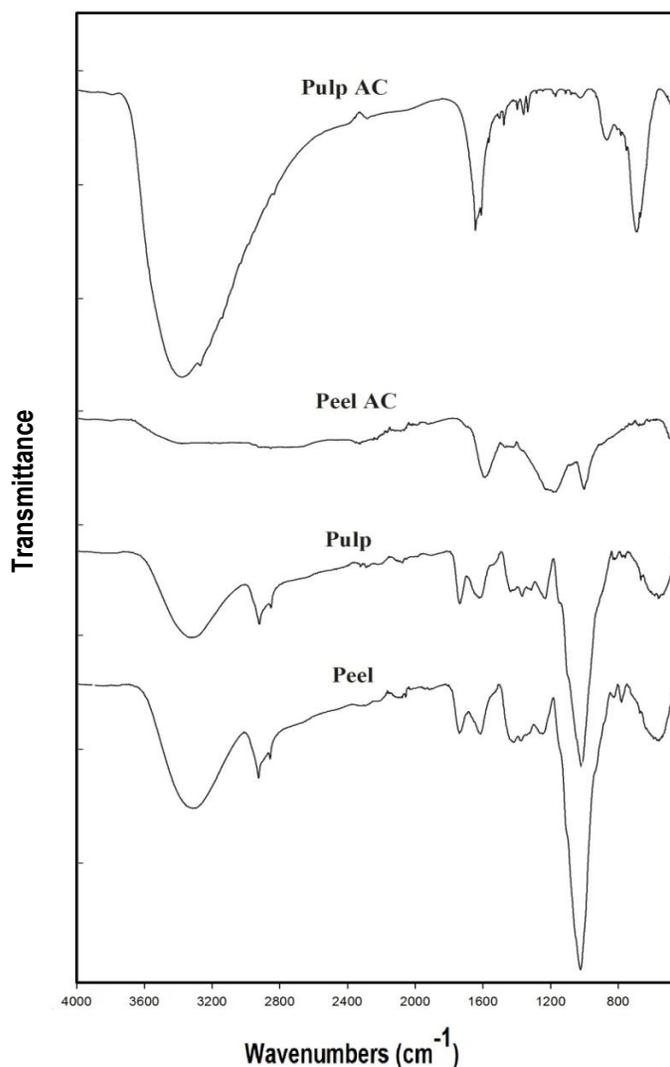
One of the important properties of adsorbents such as AC is the pore size distribution (PSD), which determines the fraction of the total pore volume accessible to molecules of a given size and shape (Deng *et al.* 2010). According to the IUPAC classification of pore dimensions, the pores of adsorbents can be classified as micropores ( $d < 2 \text{ nm}$ ), mesopores ( $d = 2 \text{ to } 50 \text{ nm}$ ), and macropores ( $d > 50 \text{ nm}$ ). Figure 7 shows the pore size distribution of the ACs calculated by the Dollimore–Heal (DH) method using the Harkins and Jura equation ( $t = [13.99 / (0.034 - \log(P/P_0))]^{0.5}$ ).

Figure 7 indicates that the pulp- and peel-based AC include some micropores (20.7 and 34%, respectively) and a large number of mesopores (73.3 and 66%, respectively) and that the peel-based ACs samples contain greater micropore content than the pulp. These results are also presented in Fig. 6, which indicates that the peel-based ACs exhibit higher nitrogen adsorption for  $P/P_0 < 0.2$  than the pulp-based ACs. The average pore diameter of the pulp- and peel-based ACs are 6.68 and 7.81 nm,

respectively, which indicate that the microwave activation process primarily produced mesopores. This high mesopore content could be attributed to the heating method. Microwave irradiation generates heat inside the particles and heats the entire particle at approximately the same rate. This uniform heating process motivates the quick diffusion of volatile matter from the inside of the AC to the surface, which increases the mesopore content.

#### *Functional groups of the activated carbon*

Fourier transform infrared (FTIR) transmission spectra were obtained to characterize the surface groups on the pulp, the peel, and the ACs prepared from these two precursors. Figure 8 shows the FTIR spectra of the pulp, peel, and pulp- and peel-based AC. The pulp and peel precursors contained many more bands than the prepared ACs. Table 4 summarizes the wave numbers and assignments of the main bands observed in Fig. 8.



**Fig. 8.** FTIR spectra: Raw pulp and peel; pulp- and peel-based ACs

**Table 4.** Wave Numbers and Ascription of the Principal Bands in the FTIR Spectra of PU, PE, and Prepared ACs

Wave number (cm <sup>-1</sup> )	Assignments	Pulp	Peel	Pulp AC	Peel AC
3500–3300	O–H Stretching (intermolecular hydrogen bonded)	*	*		
2930–2900	C–H Asym. stretching	*	*		
2720	C–H (aldehydes)			*	*
1740	C=O Stretching in esters	*	*		
1625–1610	C=C Aromatic skeletal stretching	*	*		
1580–1570	C=C Stretching band			*	*
1450–1420	C–H Asym. bending		*		
1375–1317	C–H Asym. and sym. bending	*			
1284– 1240	C–O Asym. stretching of aromatic ethers, esters and phenols	*	*		
1260–1000	C–O in carboxylic acids, alcohols, phenols and esters or the P=O bond in phosphate esters	*	*	*	*
700–400	C–C Stretching	*	*	*	*

The *apple pulp* and peel exhibit hydroxyl functional groups, including hydrogen bonding [O–H stretching (3500 to 3300 cm<sup>-1</sup>)], which is much less prevalent in both prepared ACs. The reduction of hydrogen bonding shows that the phosphoric acid acts as a dehydrating agent, reacting with the raw materials as soon as both substances are mixed (Jagtoyen and Derbyshire 1998; Suárez-García *et al.* 2002b). The intense band at approximately 2920 cm<sup>-1</sup> is assigned to asymmetric C–H stretching, which is reduced in ACs, and this indicated that the activation removed a significant amount of hydrogen. These results are in good agreement with the reduction of hydrogen shown in Table 1, which indicated that the hydrogen content decreased by 59% and 63% in the pulp- and peel-based ACs, respectively. The stretching absorption band at 1740 cm<sup>-1</sup> observed for the raw materials is associated with the carbonyl C=O. This band was absent in the prepared ACs, indicating that the chemical activation broke many bonds in aliphatic and aromatic species and eliminated many volatile and light substrates (Yagmur *et al.* 2008). The peaks at approximately 1610 and 1620 cm<sup>-1</sup> in the peel and pulp precursors result from aromatic rings or C=C bonds. The bands at 1368 cm<sup>-1</sup> for the pulp and 1414 cm<sup>-1</sup> for the peel are associated with C–H asymmetric and symmetric bending, respectively (Suárez-García *et al.* 2002b). Peaks at approximately 1582 cm<sup>-1</sup> were obtained in both prepared ACs, indicating the C=O stretching vibration of lactone and carbonyl groups (Deng *et al.* 2010b).

After activation, a significant reduction was observed for a series of complex bands in the range of 1000 to 1260 cm<sup>-1</sup> for the precursors, which includes C–O in carboxylic acids, alcohols, and esters and the P=O bond in phosphate esters (Deng *et al.* 2010b). Some weak bands were also observed in both the precursors and ACs in the range of 400 to 700 cm<sup>-1</sup>, indicating C–C stretching. MB is a basic dye, which is easily absorbed by acidic surface polarity of adsorbent. The acidic functional groups such as carboxylic, phenol, sulfonamide, and sulfhydryl (García-Gil *et al.* 2004) contribute to an acidic surface of the carbon, which promotes adsorption of basic dyes. The stretching band of C–O in carboxylic, which is an acidic group, contributes more to the interaction between the MB and the surface of the prepared ACs.

### *Comparisons with the conventional thermal method*

The microwave method of activation was compared with the conventional thermal method by which Suárez-García *et al.* (2001) prepared AC from *apple pulp* using phosphoric acid as a chemical agent. They observed a type I N<sub>2</sub> adsorption for low impregnation ratios; bent isotherms for higher impregnation ratios, which indicated pore widening; and isotherms intermediate between types I and II at higher impregnation ratios of 1.25 to 1.5 (g H<sub>3</sub>PO<sub>4</sub>/g precursor). The AC prepared by the conventional method at a high impregnation ratio of 1.5 presented a  $V_{meso}$  of 0.48 cm<sup>3</sup>/g, whereas the use of the microwave heating in this study yielded values of 1.29 and 1.71 cm<sup>3</sup>/g for the pulp- and peel-based AC, respectively. The microwave method produced more mesopores than the thermally ACs, most likely because the activation reaction under microwave radiation was more intense (Huang *et al.*, 2011). Therefore, a higher portion of mesopores (pore width  $\approx$  2-50 nm) in prepared ACs by microwave method makes these adsorbents more efficient for adsorption of MB (accessible to pores with diameters larger than 1.5 nm) compared with the conventional method. Moreover, the  $S_{BET}$  and  $V_t$  of peel-based AC (1552 m<sup>2</sup>/g, 2.59 cm<sup>3</sup>/g) are much higher than those of pulp-based AC (1103 m<sup>2</sup>/g, 1.76 cm<sup>3</sup>/g), and both of these values are higher than those for the conventionally prepared pulp-based AC at an impregnation ratio of 1.5 (914 m<sup>2</sup>/g). The higher surface areas in the microwave method were achieved in approximately 10 to 13 min, whereas the conventional method took 100 min to yield the results cited here. The short activation time using microwave heating is due to energy dissipation through dipole rotation and ionic conduction on a molecular level, resulting in energy savings and lower preparation cost compared with the conventional method. Consequently, the samples absorbed more heat in less time using the microwave method than the conventional method, leading to a higher weight loss of carbon and therefore the formation of a pore structure with a high proportion of mesopores (Huang *et al.* 2011).

## CONCLUSIONS

Large-surface-area activated carbons (ACs) were prepared from *apple pulp* and *apple peel* by microwave-induced phosphoric acid activation. The effects of different microwave power and irradiation time were investigated on physical and surface chemical properties of prepared ACs.

1. Higher microwave powers and radiation times generally facilitate the development of the pore structure. The optimum conditions are a radiation power of 700 W and a radiation time of 12.5 min for pulp-based AC and 700 W and 10 min for peel-based AC.
2. The prepared ACs primarily contains mesopores and have an acidic surface with MB adsorptions of 283.8 and 277.8 mg/g for pulp- and peel-based ACs, respectively, under optimized conditions.
3. Nitrogen adsorption data was used to calculate the BET surface areas, which were 1552 m<sup>2</sup>/g for peel-based AC and 1103 m<sup>2</sup>/g for pulp-based AC. The percentage of micropore area was 20.37% and 34% for the pulp- and peel-based AC, respectively.
4. The results show that microwave heating in AC production is more rapid, efficient, and economic than the conventional heating method, as demonstrated by the higher BET surface area, pore volume, and MB adsorption after significantly shorter activation times.

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## REFERENCES CITED

- Arami-Niya, A., Wan Daud W. M. A., S. Mjalli F., Abnisa F., and Shafeeyan M. S. (2011) "Production of microporous palm shell based activated carbon for methane adsorption: Modeling and optimization using response surface methodology," *Chemical Engineering Research and Design* 90(6), 776-784.
- Arami-Niya, A., Abnisa F., Shafeeyan M. S., Wan Daud W., and Sahu J. N. (2012) Optimization of synthesis and characterization of palm shell-based bio-char as a by-product of bio-oil production process," *BioResources* 7(1), 246-264.
- Banat, F., Al-Asheh S., and Al-Makhadmeh L. (2003). "Evaluation of the use of raw and activated date pits as potential adsorbents for dye containing waters," *Process Biochemistry* 39, 193-202.
- Barrett, E. P., Joyner, L. G., and Halenda, P. P. (1951). "The determination of pore volume and area distributions in porous substances. I. Computations from nitrogen isotherms," *J. Am. Cem. Soc.* 73, 373-380.
- Benaddi, H., Legras, D., Rouzaud, J. N., and Beguin, F. (1998). "Influence of the atmosphere in the chemical activation of wood by phosphoric acid," *Carbon* 36, 306-309.
- Budinova, T., Ekinci, E., Yardim, F., Grimm, A., Björnbohm, E., Minkova, V., and Goranova, M. (2006). "Characterization and application of activated carbon produced by H<sub>3</sub>PO<sub>4</sub> and water vapor activation," *Fuel Processing Technology* 87, 899-905.
- Daifullah, A. A. M., Girgis, B. S., and Gad, H. M. H. (2003). "Utilization of agro-residues (rice husk) in small waste water treatment plans," *Materials Letters* 57, 1723-1731.
- Daneshvar, N., Salari, D., and Aber, S. (2002). "Chromium adsorption and Cr(VI) reduction to trivalent chromium in aqueous solutions by soya cake," *Journal of Hazardous Materials* 94, 49-61.
- Deng, H., Yang, L., Tao, G., and Dai, J. (2009). "Preparation and characterization of activated carbon from cotton stalk by microwave assisted chemical activation – Application in methylene blue adsorption from aqueous solution," *Journal of Hazardous Materials* 166, 1514-1521.
- Deng, H., Li, G., Yang, H., Tang, J., and Tang J. (2010a). "Preparation of activated carbons from cotton stalk by microwave assisted KOH and K<sub>2</sub>CO<sub>3</sub> activation," *Chemical Engineering Journal* 163, 373-381.
- Deng, H., Zhang, G., Xu, X., Tao, G., and Dai, J. (2010b). "Optimization of preparation of activated carbon from cotton stalk by microwave assisted phosphoric acid-chemical activation," *Journal of Hazardous Materials* 182, 217-224.
- El-Hendawy, A., Samra, S. E., and Girgis, B. S. (2001). "Adsorption characteristics of activated carbons obtained from corncobs," *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 180, 209-221.

- Ferrero, F. (2007). "Dye removal by low cost adsorbents: Hazelnut shells in comparison with wood sawdust," *Journal of Hazardous Materials* 142, 144-152.
- Foo, K. Y., and Hameed, B. H. (2011). "Preparation and characterization of activated carbon from sunflower seed oil residue via microwave assisted  $K_2CO_3$  activation," *Bioresource Technology* 102, 9794-9799.
- Foo, K. Y., and Hameed, B. H. (2012). "Microwave-assisted preparation and adsorption performance of activated carbon from biodiesel industry solid residue: Influence of operational parameters," *Bioresource Technology* 103, 398-404.
- García-Gil, J. C., Ceppi, S. B., Velasco, M. I., Polo, A., and Senesi, N. (2004). "Long-term effects of amendment with municipal solid waste compost on the elemental and acidic functional group composition and pH-buffer capacity of soil humic acids," *Geoderma* 121, 135-142.
- Ghoreishi, S. M., and Haghghi R. (2003). "Chemical catalytic reaction and biological oxidation for treatment of non-biodegradable textile effluent," *Chemical Engineering Journal* 95, 163-169.
- Heijman, S. G. J., and Hopman, R. (1999). "Activated carbon filtration in drinking water production: Model prediction and new concepts," *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 151, 303-310.
- Hirata, M., Kawasaki, N., Nakamura, T., Matsumoto, K., Kabayama, M., Tamura, T., and Tanada, S. (2002). "Adsorption of dyes onto carbonaceous materials produced from coffee grounds by microwave treatment," *Journal of Colloid and Interface Science* 254, 17-22.
- Hoseinzadeh Hesas, R., Wan Daud, W. M. A., Sahu, J. N., and Arami-Niya, A. (2013). "The effects of a microwave heating method on the production of activated carbon from agricultural waste: A review," *Journal of Analytical and Applied Pyrolysis* 100, 1-11.
- Huang, L., Sun, Y., Wang, W., Yue, Q., and Yang, T. (2011). "Comparative study on characterization of activated carbons prepared by microwave and conventional heating methods and application in removal of oxytetracycline (OTC)," *Chemical Engineering Journal* 171, 1446-1453.
- Ioannidou, O., and Zabaniotou, A. (2007). "Agricultural residues as precursors for activated carbon production – A review," *Renewable and Sustainable Energy Reviews* 11, 1966-2005.
- Jagtøyen, M., and Derbyshire, F. (1998). "Activated carbons from yellow poplar and white oak by  $H_3PO_4$  activation," *Carbon* 36, 1085-1097.
- Oghbaei, M., and Mirzaee, O. (2010). "Microwave versus conventional sintering: A review of fundamentals, advantages and applications," *Journal of Alloys and Compounds* 494, 175-189.
- Pütün, A. E., Özbay, N., Önal, E. P., and Pütün, E. (2005). "Fixed-bed pyrolysis of cotton stalk for liquid and solid products," *Fuel Processing Technology* 86, 1207-1219.
- Rouquerol, F., Rouquerol, J., and Sing, K. (1999). "Assessment of surface area," *Adsorption by Powders and Porous Solids*, Academic Press, London, Ch. 6, pp. 165-189.
- Sing, K. S. W. (1998). "Adsorption methods for the characterization of porous materials," *Advances in Colloid and Interface Science* 76-77, 3-11.
- Suárez-García, F., Martínez-Alonso, A., and Tascón, J. M. D. (2002). "Pyrolysis of apple pulp: Effect of operation conditions and chemical additives," *Journal of Analytical and Applied Pyrolysis* 62, 93-109.

- Suárez-García, F., Martínez-Alonso, A., and Tascón, J. M. D. (2001). "Porous texture of activated carbons prepared by phosphoric acid activation of apple pulp," *Carbon* 39, 1111-1115.
- Suárez-García, F., Martínez-Alonso, A., and Tascón, J. M. D. (2002a). "Pyrolysis of apple pulp: Chemical activation with phosphoric acid," *Journal of Analytical and Applied Pyrolysis* 63, 283-301.
- Suárez-García, F., Martínez-Alonso, A., and Tascón, J. M. D. (2002b). "A comparative study of the thermal decomposition of apple pulp in the absence and presence of phosphoric acid," *Polymer Degradation and Stability* 75, 375-383.
- Thakur, S. K., Kong, T. S., and Gupta, M. (2007). "Microwave synthesis and characterization of metastable (Al/Ti) and hybrid (Al/Ti+SiC) composites," *Materials Science and Engineering: A* 452-453, 61-69.
- Thostenson, E. T., and Chou, T. W. (1999). "Microwave processing: Fundamentals and applications," *Composites Part A: Applied Science and Manufacturing* 30, 1055-1071.
- Wang, T., Tan, S., and Liang C. (2009). "Preparation and characterization of activated carbon from wood via microwave-induced  $ZnCl_2$  activation," *Carbon* 47, 1880-1883.
- Tsai, W. T., Chang, C. Y., and Lee, S. L. (1998). "A low cost adsorbent from agricultural waste corn cob by zinc chloride activation," *Bioresource Technology* 64, 211-217.
- Vadivelan, V., and Kumar, K. V. (2005). "Equilibrium, kinetics, mechanism, and process design for the sorption of methylene blue onto rice husk," *Journal of Colloid and Interface Science* 286, 90-100.
- Wang, T., Tan, S., and Liang, C. (2009). "Preparation and characterization of activated carbon from wood via microwave-induced  $ZnCl_2$  activation," *Carbon* 47, 1880-1883.
- Wartelle, L. H., Marshall, W. E., Toles, C. A., and Johns, M. M. (2000). "Comparison of nutshell granular activated carbons to commercial adsorbents for the purge-and-trap gas chromatographic analysis of volatile organic compounds," *Journal of Chromatography A* 879, 169-175.
- Xie, Z., Yang, J., Huang, X., and Huang Y. (1999). "Microwave processing and properties of ceramics with different dielectric loss," *Journal of the European Ceramic Society* 19, 381-387.
- Yadoji, P., Peelamedu, R., Agrawal, D., and Roy R. (2003). "Microwave sintering of Ni-Zn ferrites: Comparison with conventional sintering," *Materials Science and Engineering: B* 98, 269-278.
- Yagmur, E., Ozmak, M., and Aktas Z. (2008). "A novel method for production of activated carbon from waste tea by chemical activation with microwave energy," *Fuel* 87, 3278-3285.
- Zhang, Z., Qu, W., Peng, J., Zhang, L., Ma, X., Zhang, Z., and Li W. (2009). "Comparison between microwave and conventional thermal reactivations of spent activated carbon generated from vinyl acetate synthesis," *Desalination* 249, 247-252.

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