

## DEVELOPMENT OF HIGH SURFACE AREA ACTIVATED CARBON FROM WASTE MATERIAL

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### ABSTRACT

Review article on preparation of high surface area activated carbon This paper provides an overview on the methodologies for AC (activated carbon) synthesis Activated carbons with high specific surface area and pore volumes can be prepared from a variety of carbonaceous materials such as coal, coconut shell, wood, agricultural wastes or industrial wastes by physical and chemical activation method. Chemical activation gives higher carbon yield than physical activation. The highest surface area AC prepared from pistachio shells is 3895m<sup>2</sup>/g of BET surface area.

### INTRODUCTION

Activated carbon (AC) is an adsorbent produced from a variety of carbonaceous source materials. Having high surface area and porosity, it is used as an adsorbent for removal of organic compounds from air and water streams. They are also used as catalysts and catalyst supports in the catalytic processes. Therefore, high surface area and porosity are very important for AC quality because the removal of large amounts of chemical compounds from gas or liquid streams on ACs.

The qualities and characteristics of ACs depend not only on the physical and chemical properties of the initial material but also on the activation methods used. Agricultural by-products are considered as very important feedstock as they are renewable and low-cost materials. Activated carbon is a well-known material with complex pore structure, large specific surface area, good chemical stability, and various oxygen-containing functional groups on the surface. These excellent features have made it widely used in environmental protection, water and wastewater treatment, gas filters, and so forth Mesoporous activated carbon can be prepared by many methods. Traditional methods include chemical activation, physical activation, and a combination of the physical and chemical activation processes [1, 2].

raw material used for AC synthesis are wood, sawdust, lignite, peat, coal, coconut shells, and petroleum residues hardwood, coconut, bamboo, peat moss, or olive pits. A challenge in activated carbon production is to produce very specific carbons with a given pore size distribution from low cost materials at low temperature. Activated carbons with high specific surface area and pore volumes can be prepared from a variety of carbonaceous materials such as coal, coconut shell, wood, agricultural wastes or industrial wastes. Because of the high cost and non-renewable source of commercially available AC, in recent years, researchers have studied production of ACs from cheap and renewable precursors, such as olive husk, coffee endocarp, cotton stalks, plum kernels, fir wood, pistachio shell, olive stone, bamboo and flamboyant pods.

In industrial practice, coal and coconut shell are two main sources for the production of activated carbons. There are two processes for preparation of activated carbon: chemical activation and physical activation. Chemical activation is known as a single step method of preparation of activated carbon in the presence of chemical agents. Physical activation involves

carbonization of a carbonaceous materials followed by activation of the resulting char in the presence of activating agents such as CO<sub>2</sub> or steam. The chemical activation usually Takes place at a temperature lower than that used in physical activation, therefore it can improve the pore development in the carbon structure because the effect of chemicals. The carbon yields of chemical activation are higher than physical one (Ahmadpour and Do, 1997).

### LITERATURE SURVEY

H. Dolas et al.[3]has studied the Activated carbons having high surface area were produced from pistachio shells and effect of salt on surface area the hard shell was crushed into big pieces that were chemically activated using zinc chloride at room temperature and then activated in carbon dioxide gas that was saturated in water vapor. It was found that the activated carbon produced from pistachio. Shells treated 40% of sodium chloride and activated at 900 °C for 90 min has 3895m<sup>2</sup>/g of BET surface area and 5235m<sup>2</sup>/g of DR surface area and 1.86 cc/g of DR micropore volume. ZnCl<sub>2</sub>, sodium hydroxide (NaOH), hydrochloride acid (HCl) and salt (NaCl) were used for chemical activation.

However obtained ACs was carried out instrumentally. Its adsorption characterizations were determined by nitrogen adsorption at -196°C with surface area and pore size analyzer (NOVA 4000e-Quanta chrome instruments). Their surface areas were calculated from the isotherms by the Brunauer–Emmett–Teller (BET) equation their micropore volumes were calculated by using Dubinin–Radushkevich (DR) equation [20]. The ACs from 10% ZnCl<sub>2</sub> more micropores are available in its structure solution had more surface area than the others. While the amount of ZnCl<sub>2</sub> was increased, there is a decreasing of micropore volume (at range of 0.01–0.96 nm) it is seen that BET surface and micropore volumes of ACs were decreased by decreased carbonization temperature. But mesopore formation was limitedly promoted by temperature decreasing. Because of the ZnCl<sub>2</sub> concentration was increased, the radius of formed pore did not increase but the volume and the surface area of pores increased.

However, Hourieh et al. [4] studied the effect of ZnCl<sub>2</sub> concentration on the properties of AC using a raw material like pistachio-nut shell. In this study, ACs were produced from pistachio shells which were chemically activated by using ZnCl<sub>2</sub> and then physically activated by carbon dioxide passed

through water. As a result, ACs with the higher surface area were produced from pistachio shells prepared under the condition of 40% salt solution impregnation and then activated at 900 °C for 90 min. As a result, the activated carbon produced from pistachio shells treating with 40% ZnCl<sub>2</sub> then with 40% HCl in room temperature and then activated at 900 °C for 90 min has 3256m<sup>2</sup>/g of BET surface area and 3822m<sup>2</sup>/g of DR surface area and 1.36 cc/g of DR micropore volume. It was found that the activated carbon produced from pistachio shells treated 40% of sodium chloride and activated at 900°C for 90 min has 3895m<sup>2</sup>/g of BET surface area and 5235m<sup>2</sup>/g of DR surface area and 1.86 cc/g of DR micropore volume.

It can be said that ACs prepared from pistachio shells may be used for both gaseous and liquid adsorption applications depending on the different activation conditions.

K. Yang et al.[5] study the utilization of coconut shell to prepare activated carbon using agents such as steam, CO<sub>2</sub> and a mixture of steam-CO<sub>2</sub> with microwave heating. Coconut shell is the most popular and industrially widely adopted precursor for preparation of activated carbon. This has studied in order to compare the porous structure and yield of activated carbon. A two-stage activation process with carbonization at 1000 °C under N<sub>2</sub> atmosphere with conventional heating followed by activation at 900 °C with microwave heating has been utilized for preparation of activated carbon. Coconut shells Carbonization was performed in a horizontal tube furnace by electric heating and coconut shells were placed inside a stainless steel reactor. The coconut shells were heated up to a carbonization temperature of 1000 °C at a heating rate of 10 °C/min with conventional heating and were held for 2 h at the carbonization temperature under N<sub>2</sub> gas flow (100cm<sup>3</sup>/min).

The activation experiments were carried out in a self-made microwave tubular furnace, which has a single-mode continuous controllable power. Experimental series were conducted employing the flowing conditions,

A) Steam activation (1.35 g/min): to assess the effect of activation time at 900 °C;

B) CO<sub>2</sub> activation (600 cm<sup>3</sup>/min): to assess the effect of activation time at 900 °C;

C) CO<sub>2</sub>-steam mixture activation (600 cm<sup>3</sup>/min + 1.35 g/min): to assess the effect of activation time at 900 °C. selected sets of experiments were repeated to ensure the reproducibility of experimental data

BET surface area of activated carbons irrespective of the activation agent resulted in surface area in excess of 2000m<sup>2</sup>/g. The activation time using microwave heating is very much shorter, while the yield of the activated carbon compares well with the conventional heating methods. The activated carbon prepared using CO<sub>2</sub> activation has the largest BET surface area, however the activation time is approximately 2.5 times higher than the activation using steam or mixture of steam-CO<sub>2</sub>.

J. Yang, K. Qiu [6] derive the study of Activated carbons with high surface area, large pore volume, and high mesoporosity were prepared from herb residues. Preparing activated carbon from herb residues can be divided into two stages, including base-leaching and activation. The raw material was treated by 0.5M NaOH solution samples were maintained

at room temperature for 48 h and then evaporated to dryness at 105°C and activated under vacuum to a system pressure of 20 kPa using ZnCl<sub>2</sub> as the activation agent. Four activated carbons obtained under different preparation conditions were compared in detail. It was found that both the vacuum condition and base-leaching process have positive effects on the specific surface area and mesopore structure characteristics.

The Brunauer–Emmett–Teller (BET) surface area and total pore volume of the activated carbon obtained by combining vacuum condition and base-leaching method have increased by 125.3% and 64.9% respectively With an activation temperature of 450 °C and an impregnation ratio of 2.5, activated carbon with a BET surface area of 1952m<sup>2</sup>/g, a total pore volume of 1.479cm<sup>3</sup>/g, and a meso porosity of 98.0% was obtained. ZnCl<sub>2</sub> chemical activation is one of the most effective and least expensive activation methods for mesoporous activated carbon production

**Table**

The BET surface areas and pore structure characteristics of activated carbons prepared with different process conditions<sup>a</sup>.

Sample	S <sub>BET</sub> (m <sup>2</sup> /g)	S <sub>Meso</sub> (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)			Pore volume distribution (%)	
			V <sub>Total</sub>	V <sub>Micro</sub>	V <sub>Meso</sub>	V <sub>Micro</sub> /V <sub>Total</sub>	V <sub>Meso</sub> /V <sub>Total</sub>
SA	925	606	0.796	0.141	0.655	17.7	82.3
SV	1587	1232	1.067	0.117	0.950	11.0	89.0
SBA	1681	1482	1.224	0.044	1.180	3.6	96.4
SBV	2084	1626	1.313	0.139	1.174	10.6	89.4

<sup>a</sup> Note: SA-sample prepared from herb residues at atmosphere; SV-sample prepared from herb residues under vacuum; SBA-sample prepared from base-leached herb residues at atmosphere; SBV-sample prepared from base-leached herb residues under vacuum.

Both vacuum condition and base-leaching are beneficial to the specific surface area, pore volume, and mesoporosity of activated carbon. After treated with NaOH, the ash content in herb residues reduced while the volatile content increased.

The products were characterized by N<sub>2</sub> adsorption, thermo gravimetric analyzer (TGA), and scanning electron microscopy (SEM). The preparation method proposed in this study is an effective way to obtain mesoporous activated carbons with high specific surface area.

A.L. Cazetta et al [7] study the preparation of activated carbon from coconut shell with NaOH chemical reagent dried at 110 °C for 48 h, ground and granulometrically separated the raw material, which had particle size between 250  $\mu$ m and 425  $\mu$ m, room temperature to 500°C, and maintained at this temperature for 2.0 h. The obtained char was mixed

with varying amounts of NaOH pellets and 10 mL of water, at the ratios of 1:1, 2:1, and 3:1 (NaOH: char) in a vertical stainless steel reactor under magnetic stirring for 2 h and then dried at 130 °C for 4 h and observe the result as increase in the impregnation ratio (NaOH:char) caused a decrease in the yield values. And the result derived from is as follows

Textural characteristics of the activated carbons in the NaOH:char ratio of 1:1 (AC-1), 2:1 (AC-2) and 3:1 (AC-3).

	$S_{BET}$ ( $m^2 g^{-1}$ )	$V_T$ ( $cm^3 g^{-1}$ )	$V_\mu$ ( $cm^3 g^{-1}$ )	$V_m$ ( $cm^3 g^{-1}$ )	$V_\mu/V_T$ (%)	$D_p$ (nm)	Yield (%)
AC-1	783	0.378	0.356	0.022	94.2	1.63	28.9
AC-2	1842	0.927	0.775	0.152	83.6	1.80	23.4
AC-3	2825	1.498	1.143	0.355	76.3	2.27	18.8

$S_{BET}$  = BET surface area;  $V_T$  = total pore volume;  $V_\mu$  = micropore volume;  $V_m$  = mesopore volume;  $V_\mu/V_T$  = percentage of micropores,  $D_p$  = average pore diameter.

It was found that the ACs are essentially microporous and that the BET surface area was in order of 783  $m^2 g^{-1}$  for AC-1, 1842  $m^2 g^{-1}$  for AC-2, and 2825  $m^2 g^{-1}$  for AC-3 NaOH-ACs obtained from coconut shell presented good development and high BET surface area ACs. ACs are essentially microporous and that BET surface area of 2825  $m^2 g^{-1}$  was obtained for AC-3 has acid characteristics and carboxylic groups, phenolic groups and pyrone groups in its structure. This characteristic observes by FTIR analysis.

A.W.M. Ip et al. [8] prepare High surface area activated carbons from the natural biomaterial bamboo, using phosphoric acid as the activating agent. The effects of phosphoric acid impregnation ratio, activation temperature, heating rate on the carbon surface area, porosity and mass yield are presented. Activated carbons have been prepared using bamboo cane as a precursor and the properties. Three of these bamboo derived active carbons, surface areas 1337, 1628 and 2123  $m^2/g$ .

The following parameters were varied:

- Acid to bamboo ratio (1, 2, 4, 6).
- Heating rate (1 and 5  $^{\circ}C/min$ ).
- Activation temperature (600  $^{\circ}C$  and 900  $^{\circ}C$ ).

Sample name, T600/R1/X2, means that the activated carbon was produced at 600  $^{\circ}C$  with a heating rate of 1  $^{\circ}C/min$  and with an acid to bamboo ratio of 4. It show that Impregnation ratio seems to have the largest effect on the shape of  $N_2$  adsorption isotherm. Other. For carbon producing at 600  $^{\circ}C$ , decreasing the heating rate can increase the surface area. In the present study using phosphoric acid, most surface areas were greater than 1000 to over 2000  $m^2/g$  with mass recovery yields of 35–47% w/w. an activation time of 4 h and a heating rate of 1  $^{\circ}C$  per minute, which produced the highest surface area carbon of 2123  $m^2/g$ .

biomaterials converted into active carbons include; sugar beet pulp activated with carbon dioxide with surface areas 200–1300  $m^2/g$  (Mudoga et al., [9]); palm shell activated with potassium carbonate with surface areas 248–1170  $m^2/g$  (Adinata et al., [10]) and rice bran activated with sulphuric acid with surface areas 200–700  $m^2/g$  (Suzuki et al., [11]). These BET values are lower than the bamboo activated carbons produced in the present study. There are very few references in the literature referring to bamboo derived activated carbons despite the encouraging results reported in the present paper. Previous work reporting surface area values only for

bamboo carbons, include surface area values around 400–500  $m^2/g$  (Mizuta et al., [12]), steam activation produced values of 1038  $m^2/g$  (Wu [13]) and 2996  $m^2/g$  (Wang [14]).

Heating rate, impregnation ratio and activation temperature are all sensitive conditions for the surface area development. Increasing the impregnation ratio can increase the surface area initially and then decrease the surface area. For carbon production with a heating rate of 5  $^{\circ}C/min$ , increasing activation temperature can increase the surface area when the impregnation used is less than 4. The most outstanding carbon was prepared using an impregnation ratio of 2, an activation temperature of 600  $^{\circ}C$ .

Y. Sudaryanto et al.[15] author has study the preparation of High surface area activated carbon cassava peel by chemical activation.

Cassava peel is an agricultural waste from the food and starch processing industries. In this study, this solid waste was used as the precursor for activated carbon preparation. The preparation process consisted of potassium hydroxide (KOH) as chemical activating agent

Impregnation at different impregnation ratio followed by carbonization at 450–750 $^{\circ}C$  for 1–3 h. pore characteristic of carbon changes significantly with impregnation ratio and carbonization temperature. The maximum surface area and pore volume were obtained at impregnation ratio 5:2 and carbonization temperature 750 $^{\circ}C$  highest area obtain is from 1378-1605  $m^2/g$  BET surface area.

The yield of the activated carbon at carbonization temperatures more than 650  $^{\circ}C$  are less than fixed carbon in initial precursor since the potassium hydroxide is a strong base, it catalyzes the oxidation reactions. This paper study the effect of carbonization time, carbonization temp Carbonization temperature and impregnation ratio give significant effect in the pore characteristic of activated carbons produced. Following table shows derived result.

R.-L. Tseng et al. [16] this paper study the preparation of high surface area activated from carbonized corncobs (i.e., char) with KOH etching plus  $CO_2$  gasification in this work. corncob is a cheap and abundant agricultural waste of no economical value. In addition, corncob-derived ACs have been proven to be highly porous and rich in mesopores, exhibiting high adsorption capacity. Activated chars were prepared from corncob by carbonization in nitrogen.

High surface area micropore activated carbon of BET surface area of  $2595\text{m}^2\text{g}^{-1}$  and  $S_{\text{micro}}/S_{\text{p}}$  ratio of 0.899 was obtained from corncob activated with KOH [17]. Furthermore,  $\text{CO}_2$  will be utilized to develop ACs of high surface area and higher ratio mesopore for wider applications in this study. In this work comparisons were made for the physicochemical properties of the corncob carbon activated by KOH followed by  $\text{CO}_2$  gasification for different time duration. In this paper BET surface area ( $1991\text{m}^2/\text{g}$ ) of the activated carbon with KOH/char ratio equal to 1 plus 60 min of  $\text{CO}_2$  gasification is approximately equal to that ( $1976\text{m}^2/\text{g}$ ) with KOH/char ratio equal to 3 without  $\text{CO}_2$  gasification [17].

SEM observations revealed that the corncob-derived activated carbons of the group with KOH/char equal ratio to 1 were highly porous with honeycomb shaped, cottony holes, which were transformed into plain surfaces after being gasified with  $\text{CO}_2$  for 60 min. When the  $\text{CO}_2$  gasification time of the group with KOH/char ratio equal to 1 was increased from 0 to 60 min, their micropore ratios decreased rapidly from 0.805 to 0.565 and their BET surface areas rapidly increased from  $1071$  to  $1991\text{m}^2\text{g}^{-1}$ ;  $S_{\text{p}}$  values of all ACs gradually increase with increased gasification time. The BET surface area ( $2844\text{m}^2/\text{g}$ ) of cob4030 is one of the highest among the activated carbons prepared from the plant materials found so far. Less chemical dose is required for the preparation of higher surface activated carbons.

D. Huang et al. [18] in this paper, a new method, combining impregnation and vapor-hydrolysis (IVH method), would be developed to fabricate hybrid photocatalyst:  $\text{N-TiO}_2$  coated AC ( $\text{N-TiO}_2/\text{AC}$ ) with high SSA. Activated carbon (AC) is well known as one efficient support, due to its stability, mechanical resistance, high surface area and optimum porosity. Usually  $\text{TiO}_2$  is loaded on AC by CVD and sol-gel method [19, 20]

The activated carbon (AC) was impregnated into titanium tetraethoxide/urea/methanol solution, and then the impregnated AC powder was kept in water vapor at  $90^\circ\text{C}$  for 3 h for hydrolysis. Then it was calcinated to fabricate  $\text{N-TiO}_2/\text{AC}$ .

TTED was dissolved in absolute methanol, and the AC was added to the solution with stirring. After 15 min, diluted HCl solution was added, followed by the addition of urea solution (25 wt.%) under vigorous stirring. After 3 h, the water and methanol were vaporized at about  $60^\circ\text{C}$ . Then the powder was calcined at  $400^\circ\text{C}$  for 3 h to prepare  $\text{N-TiO}_2/\text{AC}$  with 8 wt.%  $\text{N-TiO}_2$

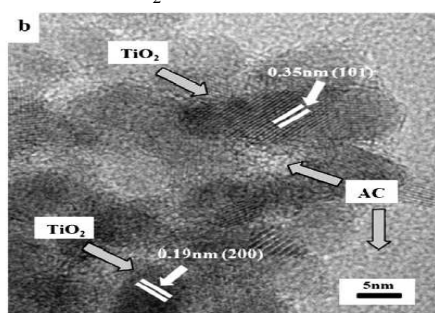


Fig. Morphologies of  $\text{N-TiO}_2/\text{AC}$ : (a) TEM image and electron diffraction pattern, and (b) HRTEM image.

when 8.3 wt.%  $\text{N-TiO}_2$  was loaded on the AC, the hybrid photocatalyst had high surface area up to  $1321\text{m}^2/\text{g}$ . The crystal structure and particle size were characterized by Transmission electron microscopy (TEM).

## CONCLUSION

In this paper from overall study it observe that Activated carbon with high surface area can be prepared from natural material and industrial waste by physical and chemical activation and it give surface area nearly equal to commercial AC or it can be further modified to get highest surface area even more than commercial AC. Heating rate, impregnation ratio and activation temperature are all sensitive conditions for the surface area development.

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