

An Overview of Activated Carbon Preparation from Various Precursors

Nur Deana Hasdi¹, Normadyzah Ahmad^{2*}, Muhammad Khairil Ahya², Siti Wahidah Puasa²

¹Qualtek Consulting Sdn Bhd, N-10-01, First Subang SS15, Jalan SS15/4G, 47500 Subang Jaya, Selangor, Malaysia

²School of Chemical Engineering, College of Engineering, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia

*Corresponding author's E-mail: normadyzah@uitm.edu.my

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ABSTRACT

Activated carbon plays an important role in the industry due to its uniqueness and special characteristics. Originally known as a good adsorbent, activated carbon has a very large surface area and high micro-porosity. Activated carbon has been widely used in petroleum, pharmaceutical, textiles and many other industries. Activated carbon can be derived directly from charcoal through chemical or physical activation. Nonetheless, activated carbon can also be obtained from other carbon precursors, such as biowaste (agricultural, municipal and industries) and natural resources (seed, leaves, fruits and barks). Generally, activated carbon can be derived from wastes through four steps; pre-processing of raw materials, thermal-conversion steps (pyrolysis or carbonization), activation, and modification. Both activation and modification were employed in the production of activated carbon to boost its adsorption performance. These steps can be divided into chemical and physical steps that help alter the physical structure of activated carbon and modify the surface chemical properties of activated carbon. Due to its reliability as an adsorbent, activated carbon has been widely used to remove pollutants in wastewater treatment and the demand for activated carbon has been increasing every year. This article reviews methods for preparing activated carbon from various precursors and discussed their performances. This review article aimed to provide recent information on efforts made by various researchers in activated carbon preparation.



Keywords: Activated Carbon; adsorbent; pyrolysis; carbonization; activation

INTRODUCTION

Activated carbon or AC is a group of porous carbons that have been activated chemically or physically. AC is usually derived from charcoal, wood, lignite, coconut shell, and other agricultural wastes. Typically, AC can be found in many forms, such as granular (GAC), powder (PAC), fibrous (ACF) and cloth (ACC)[1]. AC has a long history of usage and is well known for its effectiveness in adsorption. As early as 1500BC, AC was initially used in Ancient Egypt, where Egyptians used it for water purification and medicinal purposes [2]. AC is well-known among the carbon family due to its complexity, enhancing its porosity as an excellent adsorbent [3]. According to Yahya *et al.*[4], AC can be defined as carbonaceous material with an amorphous structure, which primarily consists of carbon elements. Because of its electronic configuration of $1s^2, 2s^2,$ and $2p^2,$ carbon has unique bonding possibilities with other elements as well as with itself. The three most possible bonds formed are hexagonal graphite, fullerene (C₆₀) and cubic diamond, as shown in Fig. 1.

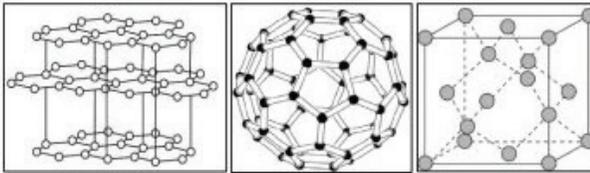


Fig. 1: Hexagonal graphite (left), fullerene (middle), cubic diamond (right) [4].

AC is categorized under graphite carbon that is non-graphitizable because of its low density attributed to its porous structure. The presence of heteroatoms, such as hydrogen, oxygen, nitrogen, phosphorus and sulphur on the surface of AC is usually used to determine its chemical properties as heteroatoms and delocalized electrons will form new functional groups during the activation of AC, which will then classify AC as acidic or base [5,6].

Syeda *et al.* [7] stated that the functional groups detected on the surfaces are carbonyl, carboxylic, ether and many more. These functional groups contain oxygen atoms, which will affect the rate of adsorption. This is supported by Ahmad *et al.* [1], who stated that stimulated active carbon has two forms – H-type and L-type. H-type carbon naturally has positive charges and possesses a hydrophobic character when being immersed in water or primed with strong acids. Meanwhile, the L-type carbon is acidic and adopts negative charges. It is hydrophilic and can neutralize strong bases. In addition, AC pore structure can be categorized into three types - micropores (< 2nm), mesopores (2nm - 50nm) and macropores (> 50nm) as shown in Fig. 2 as certified by the International Union of Pure and Applied Chemistry (IUPAC) [4,8].

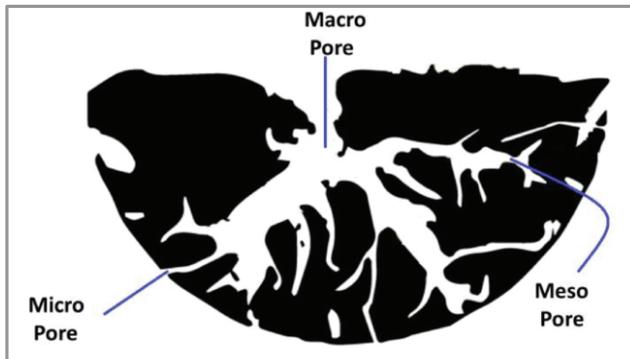


Fig. 2: Different types of pores in AC [8].

Over these years, AC has been utilized in many industrial processes, including wastewater treatment [9–12], air purification [13–15], super electrochemical capacitance as energy storage [16–18], catalyst, catalyst supports [19–21] and many more due to its unique structure, large surface area, high conductivity, and good mechanical stability.

Precursors for AC.

According to Tadda *et al.* [2], the raw materials used to produce AC usually have low inorganic contents. Jain *et al.* [22] stated that deriving AC from biowaste materials is considered a waste-to-wealth approach due to its inexpensive cost and less carbon dioxide emission compared to deriving AC from coal. Biowaste materials include industries, agricultural and municipal solid waste.

Yahya *et al.* [4] reviewed the derivation of AC from agriculture by-products resulting in the waste that can be successfully converted into a new product. The raw materials used from industrial effluent can be from the leather industry, wattle bark waste and food waste [23-25]. In addition, Liu *et al.* [26] found that expired beverages can also be used to obtain AC. Agricultural wastes used are usually coconut shell, rubber seed-shell and palm bio-waste [27–29].

Moreover, Mondal *et al.* [30] found that AC can also be derived from natural resources, such as seeds and leaves. Their research used four types of seed and three types of leaves as the precursor material to produce AC: hard whole seed, jackfruit seed, Indian rubber leaves, mint leaves and two other sources. This was supported by Koutnik *et al.* [31], who utilized herb plant species as AC sources, and Natalia *et al.* [16], who synthesized AC from areca fibres. These findings have proven that any source can be used to produce AC, if it has high carbon content and low ash content.

Methods of Deriving AC

AC can be derived through thermochemical conversion, pyrolysis or/ and activation. The activation process can be done physically or chemically. Thus, AC can be classified as pyrogenic carbonaceous matter (PCM) [2,32,33]. PCM generally refers to products of the pyrolysis process, which includes soot, chars and carbons, where the products would be useful for heating and cooking, or could be used as a catalyst and many more [33]. Fig. 3 below shows the basic steps in producing AC. A detailed explanation for each step will be explained in each subtopic.

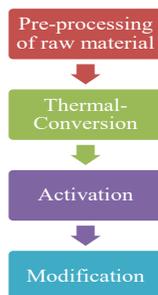


Fig. 3: Steps for Deriving AC

Pre-processing of Raw Materials

The raw materials used to derive AC should firstly undergo pre-processing steps. The pre-processing steps ensured that the sizes and forms of the raw materials are controlled [34]. Furthermore, this process is also important to remove dirt, impurities or soil attached to the raw material and draw out moisture [35–38]. The pre-processing steps are usually washed, crushed or ground as well as dried. Lastly, the sample collected would be stored in a desiccator or airtight container to prevent moisture and readily used as feed [36].

Thermal-conversion

Fu *et al.* [39] have classified two methods for chars – carbonization and pyrolysis. According to Wang *et al.* [40], pyrolysis is a traditional pretreatment process to improve biomass' physicochemical properties where it is heated in a condition of oxygen absence while carbonization is processed in the presence of inert gases at a temperature slightly lower than pyrolysis.

In his study, Yahya *et al.* [4] clarified that carbonization is the same process as pyrolysis, which was supported by Meng *et al.* [41]. Hence, it can be concluded that both carbonization and pyrolysis carry the same definition. The pyrolysis process is easier than carbonization but carbonization can also be advantageous. However, both methods affect the properties of the sample used, increasing the carbon content, reducing moisture content and improving the hydrophobic properties [40,42,43]. Therefore, pyrolysis and carbonization can be defined as the thermal degradation of materials without oxygen.

Activation

Activation is needed to enhance the pore structure of an AC [4]. Due to the intense burning action from the thermal-conversion method, some pores might be blocked by the disorganized carbon. Activation will help unclog the carbon and improve pore distribution [3]. In most of the literature, there are two types of activation; chemical and physical [3,4,34].

Physical activation includes two steps processes and usually occurs at a high temperature; from 500 °C to 1000 °C [3,4,34]. The process occurs

in an oxidizing environment, such as CO₂ and steam, where CO₂ results in a higher number of microporous pores while steam usually boosts mesoporous pores [4]. Yahya *et al.* [4] also recorded that the oxidizing gaseous forms new pores rather than enhancing the pore structure. Therefore, a higher number of pores will be produced.

Chemical activation usually runs at a lower temperature range (400 – 700 °C) [4,34]. A chemical reagent will be used for activation, such as acid [3,4,34], alkali and alkali earth metal salt [4]. The activating agent, also known as dehydrating agent, will extract the moisture content in the raw materials, decompose the lignocellulose compound, fixes the volatile component and deposit tars [4,34].

According to Yahya *et al.* [4], chemical activation can be run before the thermal-conversion steps. Chemical activation increases the yield of AC being produced. The AC produced should be washed with an acid or alkali, depending on the type of oxidizing agents used to remove the chemical components that might be absorbed into the pores. This method ensures no impurities may affect the adsorption performance [4]. This is supported by Bian *et al.* [44], where they ran chemical activation on raw materials and sludge before pyrolysis occurred. Bian *et al.* [44] also reported that after pyrolysis, a physical-chemical activation conducted on the sludge-based activated carbon (SBAC) produced higher adsorption performance.

According to Heidarinejad *et al.* [45], the chemical activation process can operate in two ways:

1. Impregnation – During this step, the raw materials or AC produced are mixed at an appropriate volume of activating agent solutions.
2. Physical mixing – For this method, the raw materials or AC produced are added with solid activating agents; the activating process will occur without water.

Hassan *et al.* [3] claimed that both chemical and physical activations have pros and cons. But recently, during activation, the thermal heating method is costly as well as consumes high energy and more time. It has been replaced with the latest invention, the microwave technique. The new technique is more specific, faster and more efficient for heating purposes [4].

Bian *et al.* [44] also stated that microwave activation is more advantageous in controlling pollution.

Modification

Despite the unique properties of AC, modifications can be done to its carbon surface to improve the AC performance. The modification process occurs on the AC's surface to modify its physical and chemical properties, such as functional groups and porous structures [46–50]. The modification of the physical structure helps in altering the pore size, whether becoming smaller or bigger, other than increasing the surface area. This method usually involves carbonization or oxidative gas to enhance the structures [47,48]. In contrast, chemical modification focuses on changing the chemical properties of AC's surface, such as the functional groups, ionic compounds, hydrophilic and hydrophobic properties. Oxidation, reduction and acid-base treatment are examples of chemical modifications on AC.

Methods to prepare AC from various sources

Activating agents may increase the versatility of AC in a wide range of applications. The chemical and physical activation processes have been widely employed to produce AC from various precursors. With the use of various activating agents, such as acid, alkali, minerals, and oxygen-rich gases, the surface characteristics of AC would be further enhanced. Furthermore, its textural properties, such as the BET surface area (S_{BET}), the total pore volume (V_{total}) and the pore diameter (d_p), are usually considered during the activation process to measure their activation performance. To summarise, the textural properties of the activated carbon prepared from various precursors at different carbonization-activation conditions are listed in Table 1.

Anthracite

Coal-based AC as a potential adsorbent is not something unfamiliar in the industry. Coal can be divided into four types; anthracite, bituminous, subbituminous and lignite. Anthracite was chosen for producing AC from coal, due to its highest carbon content [51–53].

According to Song *et al.* [53], anthracite underwent pre-processing

steps: crushing and sieving to obtain sample sizes of 1 mm and 0.5 mm. After that, the sample was dried at a temperature of 110 °C for 24 h using a stainless-steel electric toaster oven. The sample was then activated using potassium hydroxide powder at four different weight percentages; 0, 10, 50 and 100 %. Then, the sample underwent pyrolysis using a tube furnace at a 10 °C/min heating rate for 1 h in CO₂/N₂ flow with a rate of 0.2 L/min at a temperature ranging from 700, 800 and 900 °C. AC was then produced and labelled as Anthracite Activated Carbon (ACAC). Later, the ACAC sample was activated again using aqueous hydrochloric acid, HCl to draw out any activating agent in the sample to lower the ash content and enlarge the micropore volume [53].

ACAC was modified through the impregnation method using hydrobromic acid (HBr) aqueous solutions (48 %). The mass ratio used was 1:10 of ACAC: HBr, hence, 10 g of ACAC was mixed with 1 g of HBr for 12 h, respectively. The sample was then washed with distilled water to remove potassium and chloride ions before drying at 110 °C for 12 h. Lastly, the sample was dried in the oven for 12 h at a temperature of 110 °C to obtain the final bromide-impregnated ACAC sample [53].

From the research, Song *et al.* [53] obtained the optimum process condition to prepare ACAC: a carbonization temperature of 800 °C with a chemical activation of 100 % weight KOH powder. Higher temperature reduced surface area and pore volume while activation with chemical reagents increased as the weight % of the chemical reagents increased.

Physical activation can be assumed as no chemical reagents were used, thus, concluded that chemical activation is more suitable than physical ones. The highest surface area obtained by Song *et al.* [53] was 527.43 m²/g with an adsorption capacity of 2107.6 µg/g at 100 °C and 476.51 µg/g at 20 °C for mercury, Hg, adsorption in the flue gas.

Boujibar *et al.* [54] derived AC from raw anthracite (ANT-raw). Initially, the sample was washed with distilled water before being crushed and sieved to a size of 500 µm and 1000 µm. ANT-raw was chemically activated with KOH and sodium hydroxide (NaOH) with a mass ratio of 1:4 (ANT-raw to KOH/NaOH).

The sample was then heated at a temperature of 850 °C for 1 h under nitrogen flow at a rate of 600 cm³/min with a heating rate of 5 °C/min. The pyrolyzed sample was then washed with HCl (5 M) solution and distilled water to remove unwanted impurities and hydroxides. The sample was then dried once again for 24 h. Boujibar *et al.* [54] concluded that ANT-K-ACT is a better supercapacitor than ANT-Na-ACT due to their higher surface area, 2934.60 m²/g and pore volume, 1.33 cm³/g.

From these two methods, we can conclude that a coal-based AC can be derived optimally using chemical activation with KOH as an activating agent. The pyrolysis must occur at a temperature of 800-850 °C at a suitable heating and gas flow rate. Further modification may be conducted to modify the AC's structures. However, the cost of production might increase slightly in other processes.

Table 1. Comparison of textural properties of the activated carbon prepared from various precursors at different carbonization-activation conditions.

Precursors	Activation process	Activator	Carbonization activation conditions	Impregnation ratio (precursor:activator)	S _{BET} (m ² /g)	d _p (nm)	V _{total} (cm ³ /g)	Application	Ref
Anthracite coal	One-step chemical activation ^a	NaOH	T ₁ : 450°C; Time: 2 h; T ₂ : 750°C (5°C/min); Time: 2 h; Atm.: N ₂	1:4	2063	0.79	1.61	Energy and gas storage	[51]
	One-step chemical activation	KOH	T: 800°C; Time: 0.75 h; Atm.: Ar (0.33 L/min)	1:6	2260	1.97	1.11	–	[52]
	One-step chemical activation	NaOH	T: 800°C; Time: 0.75 h; Atm.: Ar (0.33 L/min)	1:6	1669	2.17	0.91	–	[53]
	One-step chemical activation	KOH	T: 800°C (10°C/min); Time: 1 h; Atm.: N ₂ (0.20 L/min)	1:1	527	–	-	Hg adsorption	[53]
	One-step chemical activation	KOH	T: 850°C (5°C/min); Time: 1 h; Atm.: N ₂ (0.60 L/min)	1:4	2935	0.75 - 2.15	1.33	Super capacitor	[54]

	One-step chemical activation	NaOH	T: 850°C (5°C/min); Time: 1 h; Atm.: N ₂ (0.60 L/min)	1:4	1200	0.90	0.50	Super capacitor	[13]
Expired beverage	Two-step chemical activation	KOH	Hydrothermal carbonization T: 180°C; Time: 4 h; Additive.: FeCl ₃ + FeCl ₂ + urea Chemical activation T: 600°C; Time: 1 h; Atm.: N ₂	40% KOH solution	1273	2.05	0.63	Methylene blue adsorption	[55]
	Two-step chemical activation	ZnCl ₂	Hydrothermal carbonization T: 200°C; Time: 4 h; Additive: Ammonia + CTAB Chemical activation T ₁ : 350°C (1°C/min); Time ₁ : 2 h; T ₂ : 800°C (2°C/min); Time ₂ : 2 h; Atm.: N ₂	1:3	1994	0.80 - 2.00	0.87	CO ₂ adsorption and super capacitor	[55]
	Two-step chemical activation	KOH	Hydrothermal carbonization T: 200°C; Time: 4 h; Additive: Ammonia + CTAB	1:4	1405	< 0.80	0.80	CO ₂ adsorption and super capacitor	[55]
Expired beverage	Two-step chemical activation	KOH	Chemical activation* T ₁ : 350°C (1°C/min); Time ₁ : 2 h; T ₂ : 600°C (1°C/min); Time ₂ : 4 h; Atm.: N ₂	1:4	1405	< 0.80	0.80	CO ₂ adsorption and super capacitor	[55]

Date palm waste	Two-step physical activation	CO ₂	Carbonization* T ₁ : 300°C (1°C/min); Time: 4 h; T ₂ : 700°C (1°C/min); Time: 2 h; T ₃ : 1000°C (1°C/min); Time: 2 h; Atm.: N ₂ (0.10 L/min) Physical activation T: 850°C (5°C/min); Time: 0.5 h; Atm.: CO ₂ (0.10 L/min)	–	546	0.60 - 1.20	0.24	–	[56]
Date palm waste	Two-step chemical activation	NaOH	Carbonization T: 600°C (5°C/min); Time: 2 h; Atm.: N ₂ (0.10 L/min) Chemical activation T: 600°C (5°C/min); Time: 2 h; Atm.: N ₂ (0.10 L/min)	1:2	655	8.17	0.15	Indigo carmine adsorption	[57]
Acai seed	Two-step chemical activation	NaOH	Carbonization Used an 8 kW fixed-bed biomass gasifier. Chemical activation* T ₁ : 400°C (5°C/min); Time: 2 h; T ₂ : 700°C (5°C/min); Time: 2 h	1:3	492	2.60	0.32	Methylene blue adsorption	[58]
	Two-step chemical activation	KOH	Carbonization T: 600°C (10°C/min); Time: 1 h; Atm.: N ₂ (0.08 L/min) Chemical activation* T ₁ : 130°C (10°C/min); Time: 12 h; T ₂ : 850°C (10°C/min); Time: 1 h; Atm.: N ₂ (0.08 L/min)	1:5	2774	2.30	1.72	Lead(II), Fe(II) and Mg(II) adsorption	[59]

Tangerine peel	One-step chemical activation	ZnCl ₂	T: 700°C; Time: 2 h; Atm.: N ₂	1:2	1230	—	—	H ₂ storage	[60]
Tangerine peel	One-step chemical activation	KOH	T: 700°C; Time: 2 h; Atm.: N ₂	1:2	447	—	—	H ₂ storage	[60]
	One-step chemical activation	H ₃ PO ₄	T: 500°C; Time: 2 h; Atm.: Inert	1:1	688	1.61 - 3.6	0.64	Acetaminiprid adsorption	[61]
	One-step chemical activation	H ₃ PO ₄	T: 600°C (10°C/min); Time: 4 h; Atm.: Inert	1:2.5	660	1.41	0.62	Carbamate adsorption	[62]
Oil palm empty fruit bunch	One-step chemical activation	H ₃ PO ₄	T: 600°C (5°C/min); Time: 3 h	—	142	< 2.60	—	Catalyst support	[63]
	Two-step physico-chemical activation	H ₂ SO ₄	Carbonization T: 400°C (10°C/min); Time: 1 h; Atm.: N ₂ (0.10 L/min) Physico-chemical activation T: 900°C (10°C/min); Time: 1 h; Atm.: CO ₂ (0.10 L/min)	1:1.5	869	1.20	0.41	Urea adsorption	[64]
	Two-step chemical activation	H ₂ SO ₄	Carbonization T: 400°C; Time: 2 h; Atm.: N ₂ (0.15 L/min) Chemical activation T: 600°C; Time: 2 h; Atm.: N ₂ (0.15 L/min)	1:10	363	1.81	48.22	Cibacron blue 3G-A adsorption	[65]
Oil palm shell	Two-step chemical activation	KOH	Carbonization T: 700°C; Atm.: N ₂ Chemical activation Microwave: 600 W; Time: 0.17 h; Atm.: N ₂	1:1.75	895	2.91	0.49	Methylene blue adsorption	[66]

Sawdust	Two-step physical activation	CO ₂	Carbonization T: 400°C; Time: 1 h; Atm.: N ₂ (0.17 L/min) Chemical activation T: 700°C; Time: 1 h; Atm.: N ₂ (0.25 L/min)	–	426	2.50	0.27	NO ₂ and H ₂ S adsorption	[67]
Sawdust	One-step physical Activation**	CO ₂	T ₁ : 740°C (10°C/min); Time ₁ : 1 h; Atm. ₁ : N ₂ (0.60 L/min) T ₂ : 740°C (10°C/min); Time ₂ : 1 h; Atm. ₂ : CO ₂ (0.60 L/min)	–	465	–	0.24	Benzene and trichloroethylene adsorption	[69]
	One-step chemical activation	KOH	T: 800°C (5°C/min); Time: 1.5 h; Atm.: Ar	1:20	1185	3.27	0.56	Super-capacitor	[70]
	Two-step chemical activation	FeCl ₃ + ZnCl ₂	Hydrothermal carbonization T: 230°C; Time: 0.5 h; Chemical activation T: 700°C (5°C/min); Time: 1.5	1:2	641	1.84	0.30	–	[71]
	One-step physical Activation**	Steam	T ₁ : 550°C (7°C/min); Time ₁ : 2 h; Atm. ₁ : Inert T ₂ : 550°C (7°C/min); Time ₂ : 0.75 h; Atm. ₂ : Steam (0.005 L/min)	–	582	2.24	0.25	CO ₂ adsorption	[72]
	One-step chemical activation	ZnCl ₂	T: 550°C (10°C/min); Time: 0.5 h	1:4	1000	2.55	0.63	Cr(VI) adsorption	[73]
Tea waste	One-step chemical activation	Potassium acetate	T: 800°C (5°C/min); Time: 1.3 h; Atm.: N ₂ (0.10 L/min)	1:2	820	2.46	0.22	Acid blue 25 adsorption	[74]
	One-step chemical activation	H ₃ PO ₄	T: 450°C; Time: 1 h; Atm.: Air	1:1.5	880	3.10	0.68	Oxytetracycline adsorption	[75]

	One-step chemical activation	KOH	T: 500°C (10°C/min); Time: 2 h; Atm.: Air	1:1	256	–	–	CO ₂ adsorption	[76]
	One-step chemical activation	H ₃ PO ₄	T: 500°C (10°C/min); Time: 2 h	1:3.5	851	3.17	0.674	Methylene blue adsorption	[77]
	One-step chemical activation	KOH	T: 500°C (10°C/min); Time: 2 h	1:3.5	306	3.07	0.24	Methylene blue adsorption	[77]
	One-step chemical activation	ZnCl ₂	T: 500°C (10°C/min); Time: 2 h	1:3.5	343	3.31	0.29	Methylene blue adsorption	[77]
Tea waste	Two-step chemical activation	KOH	Carbonization T: 400°C; Time: 1 h; Atm.: Air Chemical activation T: 600°C; Time: 2 h; Atm.: Air	–	1241	2.01	0.31	Anode electrode	[78]
Corn cob	One-step chemical activation	H ₃ PO ₄	T: 500°C; Time: 1 h	1:1	739	–	–	Catalyst support	[79]
	One-step chemical activation*	KOH	T ₁ : 400°C (10°C/min); Time: 0.5 h; T ₂ : 800°C (10°C/min); Time: 1 h; Atm.: Ar	1:2	1054	2.41	–	Hg(II) adsorption	[80]
	One-step chemical activation	H ₃ PO ₄	T: 600°C; Time: 0.3 h; Atm.: N ₂	1:2	415	3.35	0.35	Methylene blue adsorption	[81]
	One-step chemical Activation*	H ₃ PO ₄	T ₁ : 105°C; Time: 24 h; T ₂ : 450°C; Time: 1 h; Atm.: N ₂	75% H ₃ PO ₄ solution	1128	–	0.64	Catalyst support	[82]
Coconut shell	Two-step physical activation	CO ₂ + steam	Carbonization T: 800°C; Time: 5 h; Atm.: N ₂ (0.15 L/min) Physical activation T: 700°C; Time: 5 h; Atm.: CO ₂ + steam	–	610	–	–	Cr(VI) adsorption	[83]

	One-step physical activation**	Steam	T ₁ : 900°C; Atm. ₁ : N ₂ T ₂ : 900°C; Time: 1 h; Atm. ₂ : Steam	–	1137	1.91	0.48	Toluene and chloro-benzene adsorption	[84]
Coconut shell + municipal sludge waste	Two-step chemical activation	KOH	Carbonization T: 500°C (35°C/min); Time: 0.75 h; Atm.: N ₂ Chemical activation T: 800°C (35°C/min); Time: 1 h; Atm.: N ₂	1:1.5	680	3.79	0.73	–	[27]
Microalgae	Two-step chemical activation	KOH	Hydrothermal carbonization T: 222°C; Time: 0.25 h; Additive: Methanol Chemical activation T: 675°C (3°C/min); Time: 2 h; Atm.: N ₂ (0.27 L/min)	1:1.5	2099	5.90	1.20	Methylene blue adsorption	[85]
	Two-step chemical activation	K ₂ CO ₃	Hydrothermal carbonization T: 222°C; Time: 0.25 h; Additive: Methanol Chemical activation T: 675°C (3°C/min); Time: 2 h; Atm.: N ₂ (0.27 L/min)	1:1.5	2638	8.30	1.50	Methylene blue adsorption	[85]
Rice husk	Two-step chemical activation	NaOH	Carbonization T: 500°C; Time: 3 h; Atm.: N ₂ Chemical activation T ₁ : 400°C; Time ₁ : 0.42 h; T ₂ : 750°C; Time ₂ : 1.5 h; Atm. ₂ : N ₂	1:3	2176	2.54	0.91	Anode electrode	[86]

Sugarcane bagasse	Two-step physical activation	Air	Carbonization T: 750°C; Time: 1 h; Atm.: N ₂ Physical activation T: 850°C; Time: 2 h; Atm.: Air	–	99	3.07	0.07	CO ₂ adsorption	[87]
	Two-step physical activation	CO ₂	Carbonization T: 750°C; Time: 1 h; Atm.: N ₂ Physical activation T: 850°C; Time: 2 h; Atm.: CO ₂	–	622	2.42	0.38	CO ₂ adsorption	[87]
	One-step chemical activation	H ₃ PO ₄	T: 750°C; Time: 1.5 h; Atm.: N ₂	30% H ₃ PO ₄ solution	873	4.83	1.06	CO ₂ adsorption	[87]
	One-step chemical activation	NaOH	T: 850°C; Time: 1.5 h; Atm.: N ₂	30% NaOH solution	1149	6.02	1.73	CO ₂ adsorption	[87]

* Involves stepwise heat treatment **Switches of the gas atmosphere at fixed operating temperature.

Expired Beverages

Very little research has acquired AC from expired beverages, such as Coca-Cola and Sprite [26,55]. Liu *et al.* [26] reported that expired beverage was first treated by the hydrothermal reaction to prepare the sample before thermal conversion. Chemical reagents, such as ferric chloride (FeCl₃), ferrous chloride (FeCl₂) and urea were added together with the beverage before being stirred and homo dispersed. The resulting solution was then heated for 4 h at a temperature of 180 °C. Consequently, a magnetic beverage hydrothermal carbon (MBHC) was obtained, and it was then washed with distilled water and ethanol.

For activation, MBHC was impregnated with 40 % KOH solution for 6 h before being dried in a vacuum drying oven at 60 °C for 12 h. Afterwards, the sample was pyrolyzed in a tube furnace at temperatures ranging from 400 to 800 °C under N₂ flow for precisely 1 h to derive magnetic beverage activated carbon (MBAC). MBAC was then rinsed off with distilled water before undergoing further drying. The surface area obtained for MBAC was 1237 m²/g with a pore size of 2.05 nm [13].

Date palm waste

AC can be obtained from date palm petiols through 3 simple steps: pre-processing raw materials, pyrolysis, and physical/chemical activation [56,57]. According to Rezma et al. [56], initially, the petiols were washed with distilled water and dried at room temperature. The sample was then cut into smaller pieces before being pyrolyzed and activated in a horizontal tube furnace. The process condition of pyrolysis was heated up to 1000 °C at a heating rate of 1°C/min with N₂ flow of 100 mL/min.

Next, the sample was activated for 30 min under CO₂ flow with 100 mL/min flowrate at various temperatures; 750, 850 and 950 °C and a heating rate of 5 °C/min. From further porosity analysis, the optimum activation condition for the date palm petiols sample was 850 °C with a surface area of 546 m²/g [56].

Acai seed

Acai seed is mainly found in the Amazon region and has been widely used as a fuel source and agribusiness. Very little literature on the use of acai berry seed in AC production has motivated Pessôa et al. [58] to investigate its adsorptive properties in wastewater treatment. His discovery was then followed by other researchers, including Queiroz et al. [59]. As usual, the acai seed was washed and dried at 100 °C for 1 h before being ground to particle size of 0.25 mm. The ground acai seed was then carbonized at 600 °C at 10 °C/min for 1 h under 80 mL/min of N₂ flow [59].

AC derived from the acai seed underwent chemical activation with 50 % KOH solution. Two heating levels were employed; 130 °C for 720 min and 850 °C for 60 min under the same heating rate and gas flow rate as the carbonization process [59].

A further modification was done using the microwave radiation technique and nitric acid for 20 min with a power of 400 W. The modified AC was then washed with distilled water until pH 7 was obtained [59]. Further physicochemical characterization was conducted on the AC produced after activation. Modification showed that AC derived after activation with a mass ratio of 1:5 (carbonized seed to KOH) has the highest surface area,

2774 m²/g. The oxygen groups were introduced, hence, blocking the small mesopores on the modified AC. However, despite the surface area of the activated AC compared to the modified AC, the adsorption performance of the modified AC in removing metal ions in solution was higher because the AC contained a small amount of acid and primary group on its surfaces.

Queroz et al. [59] reported the presence of carboxylic, phenolic and lactonic groups created from the activation process in his study. These groups' presence have affected the surface charge in the adsorption and removal mechanism. From this, it can be concluded that adsorption performance depends not only on the surface area but also on the functional groups attached to the AC surface.

Tangerine

Like acai berry, the use of tangerine peels and seeds in AC synthesis was only reported by very few researchers [60–62]. According to Dogan et al. [60], the tangerine peel was initially washed using distilled water a few times and dried in an oven at 110 °C for around two days before being meshed and sieved into smaller particles of 100 to 500 µm size. Physical and chemical activations were done by soaking the meshed tangerine peel into zinc chloride (ZnCl₂) and KOH solution at molarity ranging from 0.1 M to 5.0 M for one day to synthesize AC from acai berry [60].

The sample was then dried in the oven for one day at 100 °C before proceeding with pyrolysis in a reactor vessel for 2 h at 700 °C under N₂ flow. The sample was then washed with NaOH and HCl to remove excess activating agents and chloride ions. The AC derived was washed with distilled water thoroughly before being dried in the oven for one day [60].

Overall, the use of ZnCl₂ was more effective due to the higher surface area achieved by AC and the higher performance at cryogenic temperatures as a hydrogen storage material [60]. For tangerine peel, despite the well-known reliability of KOH as an activating agent, the use of ZnCl₂ as an activating agent resulted in better performance in storing hydrogen due to higher surface area.

Empty fruit bunch

Unlike tangerine, empty fruit bunch (EFB), particularly from palm oil, has received much attention. Various researchers have reported the effective use of EFB in the AC synthesis in a wide variety of applications; hydrogen storage [63], water remediation [64], carbon support for catalyst [65], urea adsorption [66,67], removal of dye in aqueous solution [68] and many more. According to Ooi et al. [66], the EFB was initially shredded into fibre before being dried overnight in an oven after cleansing with nitric acid. Then, the EFB fibre was mixed with concentrated H_2SO_4 at a 1:1.5 EFB-to-acid fibre ratio. Next, the carbonization of acid-treated EFB fibre was carried out at 400 °C for 60 min and the heating rate was determined as 10 °C/min under N_2 at 100 mL/min. Afterwards, the carbonized EFB fibre was cleaned with DI Water to reduce its pH value and dried in an oven overnight at 110 °C, then, activating it with nitrogen and carbon dioxide gases. The fibre was first heated to 900 °C under N_2 gas flow at 10 °C/min and then was switched to CO_2 gas flow (flow rate was 100 mL/min) for 1 h. Afterwards, the sample was cooled down to room temperature under N_2 gas flow to yield ACF samples.

The result showed that the EFB fibre-based AC could be used as an efficient adsorbent for urea removal. The adsorptive capacity was reduced as acid-to-EFB fibre increased. This implied that the ionic repulsion force between the electronegatively charged-ACF surface and urea molecules became stronger when more OH functional groups appeared on the ACF that was prepared at a higher acid impregnation ratio [66].

Sawdust

Sawdust from various agricultural wastes has been extensively researched to synthesize AC, such as from coniferous wood [69], rubber wood [70,71], cedar wood [72], pine [73,74] and teak wood [75]. The different sources of AC, undoubtedly implied the various applications of AC derived from sawdust, including supercapacitor [72], adsorption of organic pollutants [69,71], filler of polyurethane composites [70], CO_2 capture [74] and removal of Cr(IV) [75]. Mazlan et al. [71] reported that the rubberwood sawdust was initially carbonized under N_2 gas flow of 600 mL/min for 1 h at a corresponding temperature to produce char. Subsequently, the char

was subjected to an activation process using CO₂ gas.

It was determined that the yield of AC decreases as activation temperature increases. That was because excessive heating could break the pore structure, hence, the adsorption capacity of AC for benzene and trichloroethylene was tested. Preliminary results suggested that the resultant AC derived from rubberwood sawdust could adsorb both compounds efficiently.

Furthermore, sawdust can also be used to derive GAC through hydrothermal carbonization (HTC) [73]. The sawdust was first dried at 80 °C for 2 h and ground into smaller sizes, followed by mixing the sawdust with distilled water for autoclaving at targeted temperatures with a stirring speed of 350 rpm in 30 min. Afterwards, the mixed product of hydrochar and hydrothermal solution produced was filtered to obtain the hydrochar.

The hydrochar was further dried for 1 to 2 days at 80 °C. The next step was chemically activating the hydrochar using ZnCl₂ and FeCl₃, followed by drying and pelletizing to obtain granular hydrochar (GHC). The GHC was then subjected to additional heat treatment at 700 °C at 5 °C/min. Then, the GHC was washed with 0.1 M HCl and distilled before finally drying it at 80 °C to obtain granular activated carbon (GAC). The results showed that at the optimal temperature of 230 °C, the GAC produced has a surface area of 641 m²/g and can be used for other AC applications [73].

Tea waste

Similar to sawdust, tea waste activated carbon has substantially received a lot of attention from many researchers because it is inexpensive and abundant in our society globally. Tea waste was adopted for AC production because the research on tea waste aimed to harness the potential of used tea that was usually discarded in cafes and restaurants [76]. A wide variety of applications have tested the performance of tea waste AC, including, but not limited to, the purification of biodiesel [77], oxytetracycline removal [78], the capture of CO₂ [79,80], adsorption of dyes [81,82] and battery [83]. Steps of deriving AC from tea waste (WTAC) involve both physical and chemical activation, either separately or both.

Meanwhile, Rattanaphan et al. [79] employed a combination of both chemical activation with KOH and modification with ethylenediamine (EDA) to derive AC in their study. Rattanaphan has also employed both single and two steps of the carbonization process before impregnating with KOH; i) at room temperature for 24 h, and ii) at 85 °C for 3 h by reflux technique (Refer Fig. 4). Surface modification of the AC was then carried out using EDA. 1 g of AC was immersed in 5 mL of 3 %w/v of EDA in methanol. The mixed sample was stirred at room temperature for 3 h. Then, the obtained sample was placed in a water bath and agitated at 70 °C to allow slow evaporation of the solvent. Finally, the modified WTAC with EDA was purified by overnight drying in a vacuum desiccator. The results showed that the adsorption capacity of modified WTAC was the highest at 108.97 mg/g and 78.98 mg/g for pure CO₂ and 40 % CO₂, respectively.

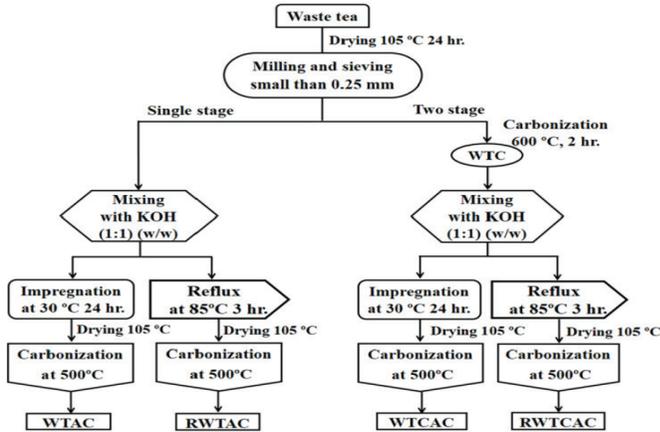


Fig. 4. The schematic illustration for preparing WTAC

Corn-cob

Deriving AC from corn cob (ACC) was initially reported by Tsai et al. [84] in 1997. Recently, ACC has received quite a handful of attention from various researchers where its applications have been diversified [85–90]. According to Duan et al.[88], the corn cob was first washed and dried at 105 °C for 24 h. It was then impregnated with phosphoric acid and activated under microwave irradiation at various concentrations. The running temperature in the first heat treatment was 105 °C for 24 h, followed

by the second heat treatment, which was microwave pyrolysis at 450 °C with a power of 700 W for 1 h under N₂ flow at 90 mL/min. The ACC was then washed with distilled water to remove excess activating agents and dried at 105 °C.

Duan et al. [88] reported that a higher H₃PO₄ concentration led to a broadening porous structure of the obtained ACC, acting as a catalyst for the production of jet fuel and gasoline. Due to that, the biogas yield was improved with the increase in H₃PO₄ concentration, pyrolysis temperature, feedstock/activated carbon catalyst ratio and the highest concentration of H₂ (69.90 vol%) achieved.

Coconut shell

Coconut shell, which is another source of agricultural waste that is commonly found in tropical countries, can also be used to synthesize AC, having an average composition of 36 % cellulose, 25 % hemicellulose and 28 % lignin [91]. Most researchers have employed similar processes in synthesizing AC from coconut shells. Pyrolysis was followed by activation or modification, depending upon its final desired functions. Chandana et al. [92] and Zhao et al. [93] employed pyrolysis in their AC synthesis. Pyrolysis was conducted at 800 °C for 5 h under pure N₂ flow at a 150 mL/min rate. According to Chandana et al. [92], the pyrolyzed sample was cooled down before being activated using CO₂ and steam, resulting in high-quality AC production with an adsorption capacity of around 26 mg/g and a surface area of 610 m²/g. Zhao et al. [93] performed an almost similar process to Chandana et al. [92], excluding activation. The activation steps used only steam for 1 h, followed by washing with HCl for 2 h. The AC was then dried and meshed into a smaller size. Compared to Chandana et al. [92], the surface area obtained by Zhao et al. [93] was higher, 1137 m²/g.

Coconut shell and municipal sludge

In addition to using a single raw material to produce AC, a mixture of two types or more raw materials can also be used. Liang et al. [27] prepared AC from coconut shells and municipal sludge. The steps were mixing the two sources at a particular weight ratio for carbonization at temperatures 300 °C to 750 °C with a heating rate of 35 °C/min. Carbonization occurred

within 30 to 120 min before activation using KOH solution. Activation was run at a certain impregnation ratio for 4 to 28 h at room temperature. The mixture was then dried for 12 h at 105 °C.

Next, the dried mixture underwent pyrolysis at a temperature of 400 to 900 °C under N₂ flow, around 30 to 120 min. Then, the final product was washed and rinsed with HCl solution and distilled water. Further drying was run at 105 °C on the resultant AC. A two-step thermal-conversion method was taken after a few experiments were run with optimum parameters. The characterization test on the AC results in surface is 680.34 m²/g with various oxygen-containing functional groups, such as C-O, O-H and C=O. These groups caused higher adsorption capacity even with moderate surface area.

Microalgae

To prepare AC from microalgae, hydrothermal carbonization (HTC) is needed to convert microalgae into algal hydrochar. The process occurs in a Parr reactor at a temperature of 222 °C for 15 min to yield 40 wt.% of hydrochar. The hydrochar obtained was vacuum filtered to separate the liquid solution, crushed and sieved to 1.18 mm for further preparation. Chemical activation using KOH was carried out on the hydrochar where it was firstly mixed and dried in the oven at 100 °C for 12 h [66].

Afterwards, the mixture was transferred into a reactor where the porous structure of the mixture was enhanced under N₂ flow with a heating rate of 3 °C/min. The temperature varied from 525 °C to 825 °C with a nitrogen flow rate of 63 to 267 cm³/min. The sample was then cooled down before being washed with HCl and distilled water. The final step was drying the sample before being commercialized as an AC.

Masoumi et al. [94] deduced that the optimum parameters for the process were 675 °C of activation temperature and 267 cm³/min of nitrogen flowrate with a 1.5 impregnation ratio. The surface area of the AC obtained was more than 2100 m²/g.

Oil palm biodiesel solid residue

Another potential precursor used for deriving AC is the oil palm biodiesel solid residue. The generation of solid residue has raised economic and environmental concerns by producing biodiesel. The oil palm shell was firstly dried, crushed and sieved into 1 to 2 mm particle size. It was then carbonized up to the temperature of 700 °C under N₂ flow. It was then followed by the activation of the sample with KOH using an impregnation ratio of 1.75 in a microwave oven with the power of 600 W for around 10 min. Lastly, the AC is washed and rinsed repeatedly using HCl and distilled water, which has a capacity of 343.94 mg/g for adsorption [95].

Rice-Husk

Yu *et al.* [96] used rice husk, which was washed using distilled water and dried overnight at 60 °C before being carbonized in a tube furnace for 3 h at 500 °C under N₂ flow, to produce AC. Then, the sample was activated using NaOH at a temperature of 400 °C for 25 min and 750 °C for 90 min. The rise in temperature was to ensure that the sample was activated. Afterwards, the activated sample was ground, washed and dried to form a porous carbon. Washing the sample with HCl will get rid of residual metal oxide, followed by rinsing with distilled water and drying at 60 °C overnight. Due to activation with NaOH, the surface area obtained increased up to 2176 m²/g.

Sugarcane Bagasse

In another study, Guo *et al.* [97] derived AC from sugarcane bagasse using different activating agents. Two simple processes were done to derive the AC using physical activation; carbonization and activation. Initially, the raw materials needed to be washed and ground into smaller sizes, followed by the activation steps. The carbonization of the sample was run at 750 °C for 1 h under N₂ flow. Next, the char formed was activated using CO₂ and air at 850 °C for 2 h.

Meanwhile, the activating agents used for chemical activation were H₃PO₄ and NaOH. The char product was impregnated with the agents for 12 h, followed by drying steps at 85 °C for 12 h. The dried mixture was then activated at temperatures of 750 °C and 850 °C under N₂ flow for 90 min.

The sample was then washed with distilled water before being dried at 85 °C for 8 h. Among the activating agents, NaOH showed the most efficient performance in adsorbing CO₂.

CONCLUSIONS

Due to the high surface area and adsorption capacity, many sources or precursors can be used to derive AC for water treatment, supercapacitors electrode, purification, and other applications. In addition, re-using waste materials in producing AC helps control environmental pollution and create a positive economy. In conclusion, to derive a high-quality AC, the raw materials should be processed first to get rid of any impurities that will affect the subsequent processing steps. Furthermore, an optimum temperature during pyrolysis and carbonization should be studied to prevent the sample from becoming only vapour or soot. Moreover, activation of the AC should be done, especially chemical activation using KOH or NaOH. These two activating agents are widely used to enlarge the AC's surface area and performance. Lastly, a modification can be done to AC if necessary but the production cost may increase slightly. Continuous research should be done on deriving AC, such as producing a more environmentally friendly technology.

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