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Exploration Sustainable Base Material for Activated Carbon Production Using Agriculture Waste as Raw Materials: A Review

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Abstract. Activated carbon can be call as “material of the future” due to its versatility usage from medical aspect, water and air treatment and a very good adsorbent characteristic. Process involved in the production of activated carbon were carbonization of raw material and activation of the charcoal to be a carbonized material. Basically the activation can be either physical or chemical activation or a combination of it. This paper is to review the potential of agricultural waste and introduce the potential base material that can be utilized as raw material for activated carbon. The process and the material selected on agricultural waste is coconut shell, palm kernel shell and rubber seed shell. The downstream industry of agricultural waste could look into material for the product development in the near future.

1. Introduction

The origin of activated carbon (AC) is associated with Ancient Egypt (1500 BC), whereby the Egyptians make use of its adsorbent characteristics for water purifications and medicinal purposes[1,2] also highlight that, in olden days (1500 B.C) activated charcoal has been used for medicinal application. Then adsorption of activated carbon was discovered in 1773 by Scheele. Activated carbon has long been recognized as one of the most versatile adsorbents to be used for the effective removal of contaminants in wastewater treatments. Charcoal is the fore runner of modern activated carbon whose ability to purify water dates back to 2000 BC [3]. Activated carbon (AC) is used in different states of applications after its discovery as a strong and reliable adsorbent. Activated carbon (AC) is a remarkable adsorbent with high specific surface area, high pore volume, and adjustable surface physical and chemical properties. It is widely used in the remediation of industrial waste water and contaminated groundwater [4,5]. An overview on AC is presented together with revisiting the sources of AC generation; methods used to generate AC comprising of pyrolysis activation; physical activation; chemical activation and steam pyrolysis [1]. The carbon element in the carbon material has a unique bonding with itself and other elements. Based on hybridization of carbon atoms, the allotropic forms of carbon are diamond, graphite,



and fullerenes. Activated charcoal is a non-graphitic and non-graphitizable carbon having highly disordered microstructure. It has high adsorption capacity because of its high surface area and porosity [2]. Figure 1 below illustrates the pore in activated carbon.

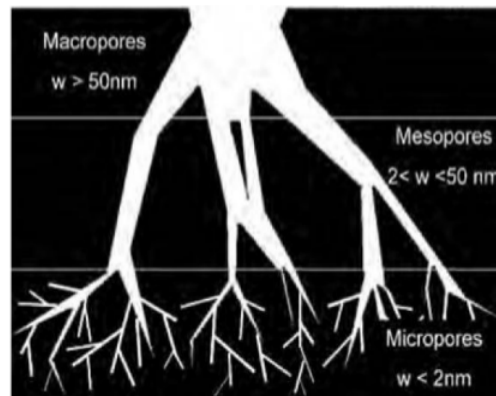


Figure 1. Structure of Activated carbon

Table 1. Classification of pore according to its size

Type of pore	Width
Micro	< 2 nm
Meso	2-50 nm
Macro	> 50 nm

The pore formation on the activated carbon was the main reason for the activated carbon adsorption ability. The statement was supported by [6] which mentioned, because of activated carbon has a large specific surface area and developed micropores, the activated carbon has a strong absorptivity and a large adsorption capacity. The physical adsorption properties of activated carbon are mainly related to the specific surface area and pore structure of activated carbon. The impurities, VOC and toxicity will bind to the pore of activated carbon due to the weak van der Waals forces and this phenomenon was called adsorption process. [7] found that the adsorption process of activated carbon is very complicated and involves the interaction of many forces (van der Waals' force, electrostatic action, complexation reaction, etc.), the surface of activated carbon contains mainly carbonyl, carboxyl, lactone and phenolic hydroxyl groups, many oxygen-containing functional groups together determine its adsorption performance. There are three main modes of action: the first is to give electrons-to be affected by electrons, the second is electrostatic action, and the third is coordination reaction. Classification of the pore were divided into 3 main group according to the size of pore formation. The pore formation can be increase throughout the activation process. Table 1 show the classification of pore in activated carbon. Another researcher [8], The total surface area of activated carbon pore wall is generally as high as 500-1700 m²/g and small micropores compared with other adsorption materials(radius<0.02 nm) is especially developed, which is also the main reason for the strong adsorption ability and adsorption capacity of activated carbon. The total specific surface area of activated carbon is determined by small micropores, and the transition pore (0.02-1 nm) plays an important role in the channel, and the large micropore (radius is 1-100 nm) is the entrance of the microsystem of the adsorption material.

2. Activated Carbon from Animal Bone

Raw material for activated carbon must have some characteristic such as low cost, abundance and eco-friendly. [9] supported this statement in his study that mentioned amidst these materials, waste materials from, saw dust, bones of animals (cow and goats), and shells of crustaceans are economical and eco-

friendly. This is due to their exceptional chemical composition, abundance, renewability, minimal cost, and efficiency in the treatment of industrial wastewater. Activated carbon can be produced using anything that were high in carbon atom, researcher from all of the world producing their activated carbon according to the raw materials that abundance in their region. Some of the using wood and other using animal bone as the raw material for the production of activated carbon. The process was the same which include carbonization process and activation process to produce high quality of activated carbon. Nworu et al. [10] mention in his study that, the bone samples of cow, donkey, chicken and horse were collected. Samples were washed and oven dried at 105°C. Accurately weighed and dried bone samples of cow, donkey, chicken and horse were carbonized in a closed crucible at 400°C, using Fisher Scientific Isotemp Muffle Furnace, for 1 hour. Another researcher mentioned that, Composite biosorbents were produced from animal bone by carbonization, activation of animal bone char with phosphoric acid and zinc (II) chloride independently, and the obtained activated carbons were separately impregnated on chitosan. The chitosan was produced from chitin, which was extracted from shrimp shell through demineralization, deproteinization and deacetylation processes [11]. The animal bone sample was collected and washed with deionized water to remove sand, dirt and flesh before being sundried. The sample was carbonized by charging into an automated muffle furnace and heated at temperature of 700 °C for 2 hours in the absence of air before it was transferred into a desiccator. For activation process, the carbonized bone was activated by crushing in a mortar. It was thereafter washed and soaked with orthophosphoric acid for 24 hours for purification and enhancement of surface area. The acid was filtered off and the crushed carbon washed several times with distilled water until pH 6-7 was achieved on the surface of the sample and the product was sundried and stored in an air tight polythene bag [12,13].

3. Selected Agricultural Waste

Malaysia were blessed with perfect climate that make almost every plantation possible to live. Based on that properties the potential of base material for activated carbon can be identified. For the purpose of this study, three type of plantation has been selected based on abundance, low cost, high density and eco-friendly. Coconut shell, palm kernel shell and rubber seed shell were selected as their obey all the influence factor. Figure 2 shows the proved of abundance of selected waste agricultural. Table 2 show the export value for coconut. Meanwhile Figure 2 and Table 3 show the Palm oil area in Malaysia and Rubber statistics respectively.

Table 2. Statistic of coconut production, area harvested and yield [14]

Element / Year	2012	2013	2014	2015	2016	2017
Production (tonnes)	624,152	624,727	595,097	504,614	504,773	517,589
Area harvested (Ha)	100,996	87,974	88,092	73,167	75,151	74,008
Yield (Hg/Ha)	61,800	71,013	67,554	68,104	67,168	69,936

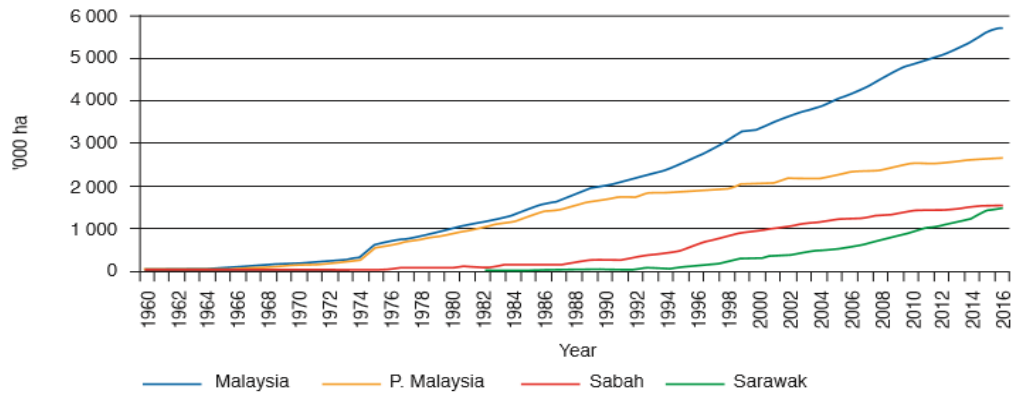


Figure 2. Palm oil plantation area in Malaysia [15]

Table 3. Rubber statistic in Malaysia [16]

Principal Statistics	September 2018	August 2019	September 2019	Change month-on-month Sept. 2019/ Aug.2019 (%)	Change yaer-on-year Sept. 2019/ Aug.2018 (%)
Production (tonnes)	48,076	57,599	61,731	7.2	28.4
EExport (tonnes)	52,365	55,879	48,058	-14.0	-8.2
Imports (tonnes)	79,811	86,977	76,578	-12.0	-4.1
Domestic Cons. (tonnes)	41,188	41,750	39,264	-6.0	-4.7
Closing stocks (tonnes)	179,351	182,695	189,454	3.7	5.6
Number of workers (estate)	11,804	11,086	11,040	-0.4	-6.5
Salaries & Wages (RM'000)	16,111	18,170	18,216	0.3	13.1

3.1. Coconut shell

Agricultural by-products and other lignocellulosic materials are particularly promising feedstocks for sustainable AC production; their use can even reduce GHG emissions by avoiding releases of greenhouse gas when they rot or are burn [14]. Coconut shell derived from the coconut plantation was most likely to be used as solid fuel. The abundancy of coconut plantation in Malaysia and its characteristic make coconut shell as good raw material for activated carbon production. Coconut shells as raw materials are utilized for activated carbon production due to their abundant supply, high density and purity, and because they seem to have a clear environmental advantage over coal-based carbons, particularly in terms of acidification potential, non-renewable energy demand and carbon footprint [17]. Coconut shells as raw materials are often utilized for activated carbon production due to their abundant supply (which improves the manufacturing economic viability), their high density and high purity [18]. Base on [19, 20], the surface area, pore volume, and pore size data for coconut shell activated carbon were describe as adsorbent pores can be classified using their pore diameter based on the definition by the International Union of Pure and Applied Chemistry as micropores (<2nm), mesopores (2–50nm), and macropores (>50nm) [20]. The average pore diameter of CSAC was found to be 2.2 nm, indicating mesoporosity. Table 4 show the previous research on coconut shell production.

Table 4. Previous research on coconut shell production.

Material	Carbonization temperature(°C)	Post Heat treatment	Activation process		Function/ element of study	Reference
			Physical	Chemical		
Coconut Shell	450	110 °C for 11 Hour	-	H ₃ PO ₄	Adsorption of reactive blue 19 dye	[21]
	450	110 °C for 2 Hour	-	H ₃ PO ₄	Electrochemical capacitors	[22]
	500	110 °C for 24 Hour	-	H ₂ SO ₄	Adsorption of textile dyes	[23]
	200	105 °C for 24 Hour	Hydrothermal process	-	Methylene blue adsorption	[24]
	-	105 °C for 48 Hour	-	KOH	Adsorption of benzene and toluene	[25]

3.2. Palm kernel shell

Palm kernel shell was one of the agricultural wastes in Malaysia, because Malaysia is one of major importer of palm oil in the world simultaneously increase the waste of palm oil plantation residue. Thus, make palm kernel shell suitable for the base material for activated carbon production. Palm kernel shell that has been predominantly found in Malaysia has been utilized as the starting material for activated carbon production [24, 26]. With more than 270 oil palm mills in the country, the total amount of palm kernel shell is equivalent to more than 2.4 million tons per annum. Comparing palm kernel shell to other solid residues from oil palm industry such as mesocarp fiber and empty fruit bunch, palm kernel shell is more competent as precursors due to its porous surface, high mechanical strength, high chemical stability, various surface functional groups, and insolubility in water [27]. Besides, poor disposal technique of these palm kernel shell including open burning and dumping at sites stimulates further utilization of these solid residues. The conventional technique for the activated carbon production is through 'physical activation' process, with steam or CO₂ as an activation agent [28]. The physical activation is defined as a dual-step process that starts with carbonization (pyrolysis) in presence of inert gas and is followed by activation of the resulting char. Table 5 show the previous research on Palm shell production.

Table 5. Previous research on Palm shell production

Material	Carbonization temperature(°C)	Post Heat treatment	Activation process		Function/ element of study	Reference
			Physical	Chemical		
Palm shell	500-550	110 °C for 24 Hour	-	ZnCl ₂	Dye removal	[29]
	800-1000	100 °C for 3 Hour	Steam generator	-	Removal of pollutant and POME treatment	[30]
	500	110 °C for 24 Hour	Steam generator	-	Adsorption of heavy metal	[31]
	950	100 °C for 2 Hour	steam	KOH	Methylene blue adsorption	[32]
	-	110 °C for 12 Hour	-	ZnCl ₂	Adsorption of methane	[33]

3.3. Rubber seed shell

Rubber seed shell contain high carbon in its shell, these could be utilized as base material for activated carbon. [34-36]. Rubber seed-shell has high carbon content with high potential to be the precursor of activated carbon production. Malaysia have large number of rubber plantation. Basically, the rubber its self is being used, the seed of the rubber will remain on the ground without any further usage. Thus, these studies will help to utilized and process the rubber seed shell as activated carbon. [37,38] also supported the idea which mentioned that, In Thailand, rubber tree is the economic crop exported in the form of rubber smoked sheets, latex and crepe rubber. Its waste is used as the feedstock for the other industrial products. Rubber seed shell is the residue from the oil extraction of rubber seed for biodiesel production. Activated carbon prepared from rubber seed shell by using KOH as the activating agent via two different methods. Influence of alkaline concentration on the product property was investigated. Table 6 show the previous research on rubber seed shell production.

Table 6. Previous research on rubber seed shell production

Material	Carbonization temperature(°C)	Post Heat treatment	Activation process		Function/ element of study	Reference
			Physical	Chemical		
Rubber seed shell	500-700	100 °C for 12 Hour	-	KOH	Removal of Cu ²⁺ and Zn ²⁺	[35]
	-	100 °C for 24 Hour	-	ZnCl ₂	Surface area and pore size	[36]
	400-600	105 °C for 24 Hour	-	H ₃ PO ₄	Quality of Activated carbon by temperature	[37]
	600-700	-	-	Chitosan	Removal of Cu ²⁺ and Pb ²⁺	[38]
	100	80 °C for 6 Hour	Superheated vapour	-	Effect of environmental friendly	[39]

4. Conclusions

This study will emphasized more about the process of activated carbon production and highlight about the potential material that could be utilize for the activated carbon production. In conclusion this topic was highlighted the potential of agricultural waste to be activated carbon base materials. This review also helps future researcher with the specific element such as the understanding of each stage in production of activated carbon, type of activation process either physical, chemical or combination and the selection of appropriate process for sustainable development.

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