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RESEARCH ARTICLE

Synthesis of Activated Carbon from *Adonidia merrillii* Seeds

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ABSTRACT

This research paper presents a novel approach to the production of activated carbon (AC) utilizing *Adonidia merrillii* seeds, a readily available biomass resource. The study outlines the step-by-step process of activation, including preparation, activation, and characterization of the resulting AC. The ACs were prepared by carbonization method which was then followed by activation of carbonized *A. merrillii* seeds. $ZnCl_2$ was used as the activating agent at an impregnation ratio of 1:10 wt/vol. Physicochemical properties, such as surface area, pore size distribution, and adsorption capacity, were extensively analyzed. From the XRF analysis, the elemental composition of merit of the AC is potassium chloride known as sylvite, 0.435; calcium oxide also known as lime, 2.850; chloroapatite, 2.850; silicon dioxide, also known as quartz, 1.669; and γ-anhydrite, 1.405. The X-ray diffraction analysis conducted on the AC showed that sylvite had the highest percentage of 25%, Lime, 22.5%, chloroapatite, 17.3%, quartz, 19.3%, and anhydrite with the least percentage of 15.6%. The results demonstrate the potential of *A. merrillii* seeds as a sustainable precursor for producing AC with desirable properties for various applications.

Key words: Activated carbon, *Adonidia merrillii* seeds, adsorption, biomass precursor, environmental applications

INTRODUCTION

Activated carbon (AC) has gained considerable attention due to its versatile applications in water treatment, air purification, and adsorption-based processes. This study explores the synthesis of AC from *Adonidia merrillii* seeds, aiming to utilize a natural and abundant precursor for producing effective adsorbents. The abundance and availability of agricultural by-products make them good sources of raw materials for AC production. AC production from agriculture waste materials has attracted researchers in recent years.[1] AC is a non-graphite form of carbon that could be produced from any carbonaceous material such as coal, lignite, wood, paddy husk, coir pith, and coconut shell. AC is a unique and effective agent for purification and for isolation and recovery of trace materials. During the last two to three decades, treatment with active carbon has become an important unit process for separations and purifications in the food, pharmaceuticals, sugar, chemical, and other processing industries.[2] Over the last few decades, adsorption has gained importance as a purification, separation, and recovery process on an industrial scale. AC is perhaps one of the most widely used adsorbents in industry for environmental applications. ACs are carbons of highly microporous structure with both high internal surface area and porosity, and commercially, the most common adsorbents used for the removal of organic and inorganic pollutants from air and water streams.[3] Numerous wholesome products are produced from palms, which include the popular *A. merrillii*, *Elaeis gunneensis*, *Cocus nucifera*, *Phoenix dactylifera*, and several palm lipids. Fats and oils (lipids) which are naturally

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occurring in plants or animals are molecules that are soluble in organic nonpolar solvents.[4] *A. merrillii,* syn. *Normanbya merrillii* (Becc.), or *Veitchia merrillii* (Becc.) *H. E. Moore (Arecaceae)* is generally identified to be Adonidia palm, Manila palm, or Christmas palm. Palms represent the third chief important plant family for human use. There is still an inadequate study on the industrial applications of some palm trees.[5] *A. merrillii* is an ornamental palm widely cultivated for its exotic appearance. *A. merrillii* is among the most widespread ornamental palms in the world today. However, the seed oil is not yet utilized like other seed oils, for industrial application. The molecules of lipids contain a bulky portion of hydrocarbon and less polar functional groups, and this explains their solubility nature.[6] Fats exist as solid or semi-solid triglycerides at room temperature while oils exist as liquid triglycerides at room temperature. It is known that fat and oil make the major three classes of food after carbohydrates and are considered an essential nutrient in our diet.[7] The Christmas palm, also known as the *A. merrillii*, plays an important role in tropical landscapes because few other palm species are so well suited for small sites. These palms are self-cleaning, meaning that once an old leaf has died, it will drop off cleanly by itself. However, unless the attractive red fruits are desired. Various efforts have been made to accelerate the germination of Christmas palms through the use of chemicals that can accelerate the germination of Christmas palm seeds including H_2SO_4 and KNO_3 treatment.[8] *A. merrillii* flowers are inconspicuous, creamy-white, unisexual, and occur in clusters of 2–3 or solitary along the rachillae in twisted spikes. Staminate flowers are bullet shaped, with three imbricate sepals, three valvate petals longer than sepals, 45–50 stamens with long slender filaments and dorsifixed anthers, and with a trifid or bifid pistillode. Pistillate flowers, ovoid, with three imbricate sepals and three petals, slightly longer than sepals, six connate staminodes, gynoecium ovoid, unilocular, uniovulate, style thick, stigmas three sessile. Fruit ovoid, 3–4 cm long, beaked, pale green becoming bright red at maturity, perianth whorls enlarged, persistent, stigmatic remain apical. The fruit has a thin epicarp and dry, yellowish, fleshy mesocarp, and thin, fragile endocarp. Seed is ovoid, truncate basally, pointed apically, with ruminate endosperm and embryo basally. It is perennial, seed propagated, tree, and Woody.[9]

A. merrillii is among the most widespread ornamental palms, when matured the seed falls off as waste and contributes to pollution. The wasted seeds are therefore used in the production of AC. Almost any organic matter with a large percentage of carbon could theoretically be activated to enhance its adsorption capacity. In practice, however, the best sources of AC should have a high carbon content, a long storage life, are hard enough to maintain their properties under usage conditions, are obtainable at a low cost, and be capable of producing a high-quality activated product when processed.[10] Of all these parameters, cost is very important when comparing sorbent materials. Unfortunately, cost information is seldom reported, and the expense of individual sorbents varies depending on the degree of processing required and the local availability of raw materials. In general, an adsorbent can be termed as of low cost if its source requires limited processing, is abundant in nature, or is a by-product or a waste material from another industry. Considering the aforementioned aspects, there has been a switch of interest from the use of traditional raw materials to agricultural wastes and by-products as precursors for AC.[11] Production of AC from agricultural waste and by-products has potential economic and environmental advantages for countries where agriculture is the main economic activity. This is because, first, it converts unwanted, low-value agricultural waste to useful high-value adsorbents. Second, it provides an excellent method for agricultural solid waste management thereby reducing environmental pollution. Third, it can reduce the importation of AC and thereby increase the economic base in the country.[12]

Agricultural waste and by-products can be used for the production of AC with a high adsorption capacity, considerable mechanical strength, and low ash content.[12] A literature survey reveals a huge amount of information on the potential of agricultural wastes as raw materials for the production of commercial AC.[11] Various types of agricultural wastes and by-products have been studied depending on their local availability. Materials that have drawn much interest include nut shells and stones, seed hulls/husks, plant straws/stalks, sugarcane bagasse, agro-forestry residues such as sawdust, etc.[10] Physical activation of carbonized char is normally accomplished using gaseous activating agents at elevated temperatures. The most common activating agents are steam, carbon dioxide, and air or their mixtures. However, CO_2 is widely preferred because it is clean, easy to handle and it facilitates control of the activation process due to the slow reaction rate at temperatures around 800°C. During the activation process, disorganized carbon is burnt out and the closed and clogged pores between crystallites are freed. By the removal of disorganized carbon, the surface of the elementary crystallites becomes exposed to the action of the activating agent. The removal of non-organized carbon and the non-uniform burn-off of elementary crystallites leads to the formation of new pores and to the development of the macroporous structures. This is followed by the widening of existing pores or the formation of larger pores by the complete burn-off of walls between adjacent micropores.[13]

ACs from rice husk, corn cob, oak, corn hulls, corn stover, rice straw, pecan shells, peanut hulls, cashew nut shells, coconut shells, almond shells,[14-19] black wattle wood charcoal,[20] and palm fruit shells[20] have been prepared using the physical activation method. The raw materials were carbonized under an inert atmosphere and then activated at temperatures ranging from 400 to 850°C and sometimes up to 1200.[17] Most organic substances with high carbon content are potential raw materials for AC production. To produce a porous carbon structure, the under-listed factors are, high carbon content, low inorganic content (i.e. low ash), potential extent of activation, low degradation upon storage, high density and sufficient volatile content, stability of supply in the countries, and inexpensive materials.[21] The activation time also has a greater influence on both the carbonization process and properties of AC in addition to their hardness, volatile content, and relatively high density, and content, which make them most prepared for hard GAC production. Moreover, other materials for example coconut shells, olive stones, and peach waste are commercially utilized for micro-porous AC production and as well find usage for a variety of applications.[21] In AC production, the activation temperature plays a vital role in affecting the characteristics of the AC produced. As for commercial purposes AC, it is normally carried out in a mixture of steam and CO_2 at a temperature above 800°C. In recent times, researchers have been up-and-doing to optimize the final activation temperature to reduce the cost and period of AC production. Several studies have been reported which indicated that activation temperature has a great influence on surface area and production yield of AC.[22] The activation temperature is between 200 and 1100°C. However, a temperature range of 400–500°C was reported by previous researchers to be considered regardless of the time taken and the impregnation ratio for a variety of raw materials. Therefore, increasing activation temperature always results in the reduction of AC yield during production, which at the same time results in increasing the volume of volatile substances released.[22] The availability of good surface area of particles possessed by AC as well as its adsorptive ability makes it a significant constituent in many industries. Industries such as petroleum, fertilizer plants, nuclear, pharmaceuticals, cosmetics, textiles, automobiles, and vacuum manufacturing all uses AC.[11] AC is a good porous material, which made it very effective in the adsorption of solutes from aqueous solutions. This was suggested to be due to the possession of a large specific surface area. Furthermore, it has been extensively used for solvent recovery, separation of gases, dye removal from industrial wastewater, and as a catalyst in the process of biodiesel production. In addition, AC produced from agricultural wastes' biomass could also be useful in the adsorption and control of air contaminants such as in the treatment of industrial gas emissions. Still, AC can be used for gas separation, purification, and deodorization serving as a catalyst due to the possession of high surface area and multiple numbers of micropores while for liquid phase adsorption AC can be used in many purification processes such as wastewater treatment, which happens to be among the most relevant. Other applications are the purification of drinking water, treatment of industrial effluents, and groundwater treatment. Adsorption of pesticides and nitrate from surface water can also be achieved by the use of AC.[23]

MATERIALS AND METHODS

Materials

Raw Material Collection: Mature and dried *A. merrillii* seeds were collected from the premises of the Akwa Ibom State University, Ikot Akpaden

Campus. Other materials used include Condenser, Reactor, Hose, Thread tape, and Paper tape. The seeds were cleaned to remove any impurities or foreign substances.

Methods

Preparation of AC

The AC preparation method of Savova *et al*.[20] was used. *A. merrillii* palm collected after discarding the fruit pulp, was sun dried, crushed, and grinded in a ball mill. The grinded sample was sieved to obtain the particles of uniform size, 1.0–1.5 mm. The precursor obtained was washed to remove surface bounded impurities and mud and dried at 100°C. The schematic diagram for the preparation and activation of AC is shown in Figure 1.

Proximate Analysis

The moisture content was determined by oven-drying test method (ASTM D2867-09). A sample of carbon was put into a dry, closed capsule (of known weight), and weighed accurately. The capsule was opened and placed with the lid in a preheated oven. The sample was dried to constant weight, then removed from the oven and with the capsule closed, cooled to room temperature. The closed capsule was weighed again accurately. The percentage difference of weight was expressed as the moisture content of the sample. The percentage of volatile matter of the AC samples was determined by the standard method (ASTM D5832-98). The percentage of weight loss was regarded as the percentage of volatile matter. Fixed carbon is a calculated value and it is the resultant of the summation of percentage moisture, ash, and volatile matter subtracted from 100.

$$\text{Fixed carbon (\%)} = 100 - (\text{moisture, \%} + \text{ash, \%} + \text{volatile matter, \%}) \quad (1)$$

Yield

The yield of AC was calculated on a chemical-free basis and can be regarded as an indicator of the process efficiency of the chemical activation process. The yield of AC is calculated as the percentage weight of the resultant AC divided by the weight of dried *A. merrillii* seeds.

$$Yield\ (\%) = \frac{weight\ of\ acitvated\ carbon\ after\ carbonization}{weight\ of\ the\ raw\ material} \times 100 \quad (2)$$

Bulk Density

The bulk density (r) of the AC was estimated using a pycnometer. Initially, the weight of the pycnometer with the inserted AC sample ($m_o + m_{AC}$) was measured. Then, the pycnometer filled up with water and the weight of water m'_{H2O} (measured weight minus $m_o + m_{AC}$) was noted. The volume of added water V'_{H2O} obtained as

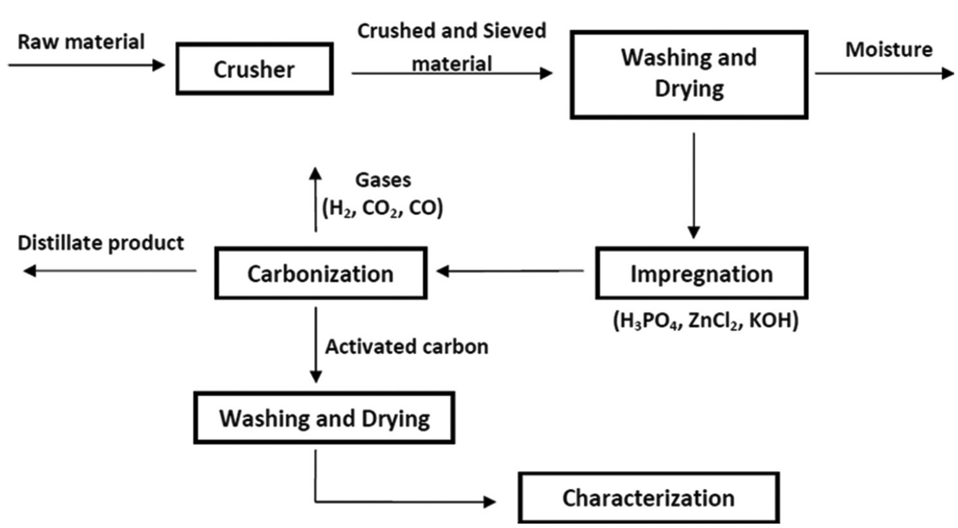

Figure 1: Schematic diagram for preparation of AC

$$V'_{H2O} = \frac{m'_{H2o}}{\rho_{H3o}} \quad (3)$$

Carbonization

The cleaned seeds were carbonization, and the biomass was heated in an oxygen-limited environment to eliminate volatile compounds and leave behind carbonized material. The carbonization process was carried out in a muffle furnace at 450°C temperature for 8 h.

Activation

The carbonized *A. merrillii* seeds were activated to create a porous structure, thereby increasing the surface area and adsorption capacity of the final product. Zinc chloride ($ZnCl_{2)}$ was used as an activating agent to study its influence on the AC's properties. Different activation temperatures and times were also used to explore and optimize the activation process.

Characterization

The produced AC was characterized using various analytical techniques, including scanning electron microscopy (SEM) used to determine the images of the microstructure and surface morphology of both the *A. merrillii* seed and the AC, X-ray powder diffraction, was used to analyze the crystallographic structure of the AC, Fourier-transform infrared spectroscopy. These analyses will help to assess the structure, morphology, and surface chemistry of the AC.

RESULTS AND DISCUSSIONS

Characterization of AC

Table 1 indicates the mass of the ash content in (g), the contact time taken for the characterization at an impregnation ratio of 1:10 wt/vol at a constant temperature of 450°C. A straight line graph was obtained against contact time [Figure 1]. At the highest mass of 50 g, the contact time taken was approximately 2 h. The total time taken for the characterization of *A. merrillii* was approximately 8 h (479.43 min).

Table 1: Characterization of AC

Mass (g)	Contact time (min)	Temperature (°C)
50	122.09	450
40	103.00	450
30	90.02	450
20	83.00	450
10	81.04	450

From Figure 2, the result shows that activation time increases as the mass of the *A. merrillii* ash increases. The result obtained is similar to the study of Olatunji[25] on the preparation of AC from the pyrolytic conversion of *Musa paradisiaca*. In his study, it was observed that the ash content of each of the impregnation ratios of different activating agents was high because it ranged from 33.6% to 39.4%.

X-Ray Diffraction Analysis

From the table 2, the composition of AC produced from *A. merrillii* seed includes sylvite with the highest percentage of 25%, lime (22.5%), chlorapatite (17.3%), quartz (19.3%), and anhydrite with a percentage of (15.6).

From Figure 3, sylvite dominates the other minerals with 25 (3%) occurrence in the AC produced. Sylvite is an evaporite mineral of composition KCl. It is a member of the halide group and is a relatively common mineral in saline environments due to its high solubility, sylvite is not an important mineral in most soils maintained under natural conditions; however, its use as a fertilizer, but it does not persist for any substantial period in humid region soils according to Warr.[26] Lime has the second highest percentage composition of 22.5 (10%) [Figure 4]. Lime is a calcium-containing inorganic material composed primarily of oxides and hydroxide,

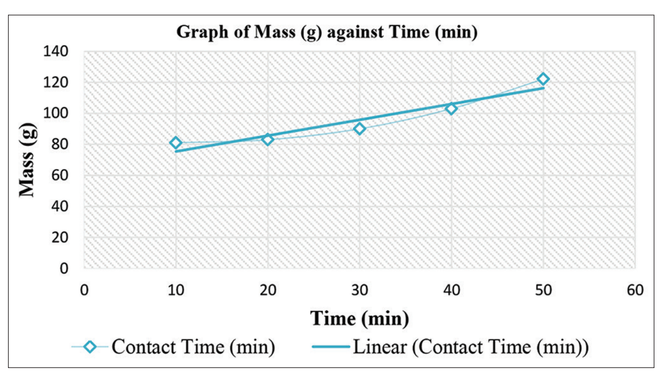

Figure 2: Graph of mass against time

usually calcium oxide and/or calcium hydroxide. The International Mineralogical Association recognizes lime as a mineral with the chemical formula of CaO. It is used extensively for wastewater treatment with ferrous sulfate.[27]

Anhydrite has the lowest composition value of 15.6% followed by chloroapatite which has a composition value of 17.3 and Quartz with a composition value of 19.3.

The peaks of the residual phase of *A. merrillii* composition shown an indexed in Figure 4, there is a major peak at 28°. The X-rays are collimated and directed to a nanomaterial sample, where the interaction of the incident rays with the sample produces a diffracted ray, which is then detected, processed, and counted. The intensity of the diffracted rays scattered at different angles of material is plotted to display a diffraction pattern. The structural property of the sample examine by X-ray diffraction shows that the AC produced from *A. merrillii* is crystalline in nature.

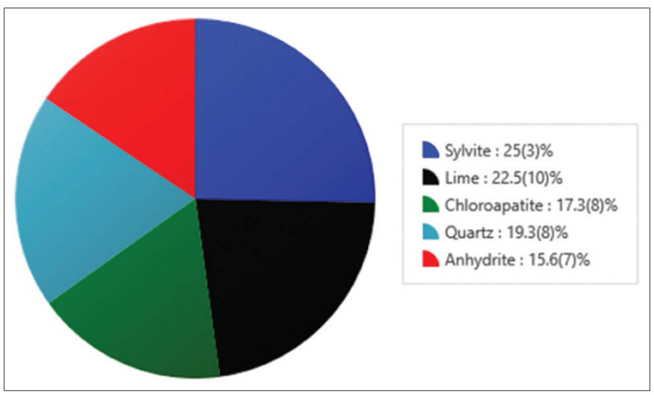

Figure 3: Pie chart representation of AC compositions

XRF Analysis

Further qualitative analysis was done on the AC, and this was to determine the elemental compositions of the AC produced from *A. merrilli*. The energy of this X-ray is equal to the specific difference in energy between the two quantum states of the electron. The measurement of this energy is the basis of XRF analysis as shown in Table 3.

In Table 3, the qualitative figures of merit are listed. $Ca_{10}Cl_2$ (PO_4) and CaO had the figure merit of 2.850, respectively, followed by SiO_2 with a value of 1.669. Potassium chloride has the least figure of merit value of 0.435. The results show that sylvite deems to be the highest mineral composition in the AC. Similarly, Figure 5 shows the phase data view of the activated carbon produced which shows the elemental composition of the AC includes potassium chloride known as sylvite, calcium oxide, CaO, also known as lime, silicon dioxide, also known as silica, most commonly found in nature as quartz and calcium sulfate-related hydrates, it is in the form of γ-anhydrite (the anhydrous form).

SEM analysis

The SEM of the adsorbents from the AC are shown in Figure 6 below at different magnifications,

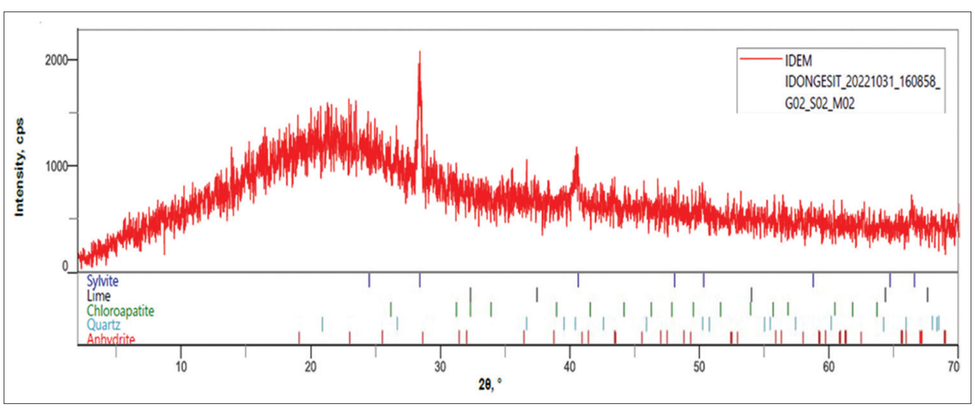

Figure 4: XRD peaks of thin film of *Adonidia merrilli*

Table 2 : The result obtained from the X-ray diffraction analysis

Dataset/weight fraction %	Value unit	Sylvite	Lime	Chloroapatite	Quartz	Anhydrite
Adonidia merrilli (AC)	0	25 (3)	22.5 (10)	17.3 (8)	19.3 (8)	15.6 (7)

Table 3: Qualitative analysis of X-ray fluorescence

Phase name	Formula	Figure of merit	Space group	DB card number
Sylvite	KCl	0.435	225: fm-3m	00-001-0786
Lime	CaO	2.850	225: fm-3m	00-003-1123
Chloroapatite	$Ca_{10}\,Cl_2\,(PO_4)$	2.850	-	00-001-1011
Quartz	SiO_2	1.669	154: p3221	00-001-0649
Anhydrite	$Ca\,(SO_4)$	1.405	63:Bbmm	01-074-2421

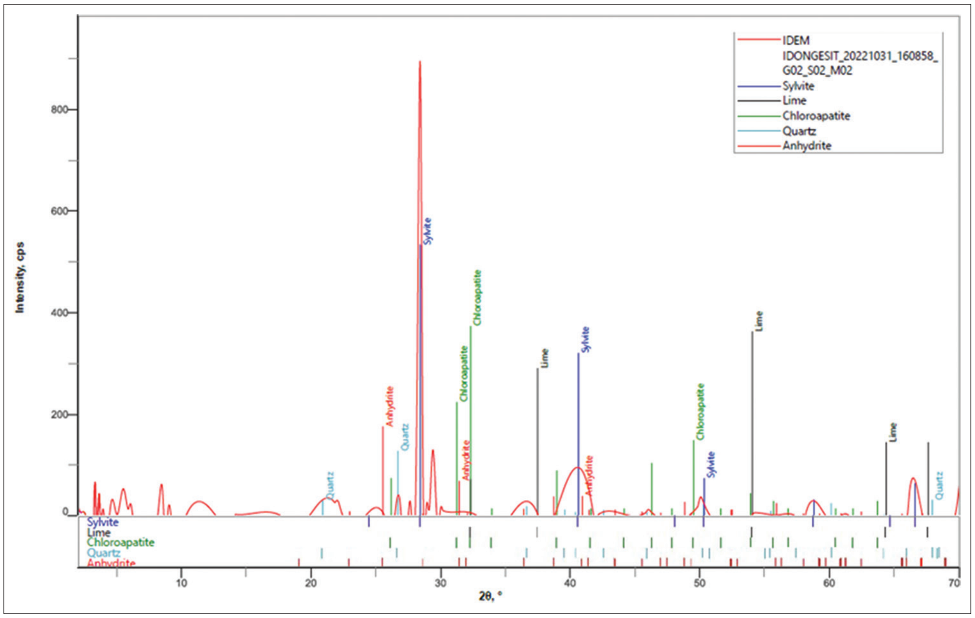

Figure 5: Phase data view

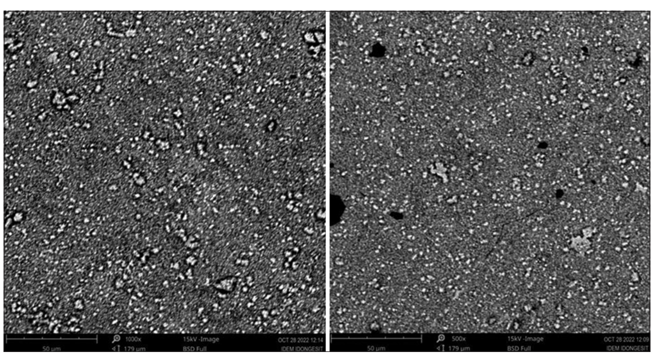

Figure 6: SEM analysis result

depicting that those adsorbents all possess a rough and heterogeneous surface morphology.

CONCLUSION

AC obtained from *A. merrillii* seeds has some advantages like low cost as well as less stressful procedure. The result from the X-ray diffraction, X-ray florescence, and SEM has shown that *A. merrillii* seed is a carbonaceous material. The AC produced from *A. merrillii* seeds can be used as adsorbents in the industry for environmental applications, it is highly microporous in structure with high internal surface area and porosity, and commercially can be used as adsorbents for the removal of organic and inorganic pollutants from air and water streams.

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