PREPARATION AND CHARACTERIZATION OF ACTIVATED CARBON FROM *Moringa Oleifera* SEED POD

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ABSTRACT: *Activated carbon (AC1 – AC3) were successfully produced from Moringa oleifera seed pod by chemical activation method ($ZnCl_2$ and H_2SO_4) at 600 ^{0}C and 800 ^{0}C in furnace supplied with nitrogen gas. Electrochemical, thermal and morphology of activated carbon properties were analyzed based using TGA, SEM, FTIR, elemental analysis (CHN). Adsorption capacity of methylene blue (dye) and 4-chlorophenol were determined as function of adsorbate initial concentration and adsorbent dosage. Optimum condition for producing activated carbon (AC3) from Moringa oleifera seed pod was activated at 800 ^{0}C using $ZnCl_2$ as activating agent resulting BET surface area 853.68 m^2g^{-1} and pore diameter 2.13 nm. Adsorption experiment showed that AC3 able to remove 90.7 % of methylene blue solution (2 x 10^{-3} M) and 97.4% of 4-chlorophenol (66.95 ppm), respectively. Finding showed that Moringa oleifera seed pod has the potential to be a promising precursor for the production of activated carbon.*

Keywords: Moringa, activated carbon, chemical activation, adsorption

1. INTRODUCTION

Adsorption is widely used an effective physical method of separation in order to eliminating or lowering the concentration of wide range of dissolved pollutants in an effluents. Activated carbon is well known adsorbent. *What is Activated carbon?* Activated carbons is porosity (space) enclosed by carbon atoms. It is microcrystalline, non-graphite form of carbon with porous structure that has been processed to develop its internal porosity [1]. AC consist of 87 – 97% carbon, C and other elements (H,O,S,N).

Activated carbon is applied widely in a variety of fields such as food and chemical industries, wastewater treatment, solvent recovery, air pollution control and hyrometallurgy for the recovery of gold and silver [2]. Adsorption on activated carbon has been found to be more effective compared to other chemical and physical methods for wastewater treatment in terms of its capability for efficiently adsorbing a broad range of pollutants, and fast adsorption kinetics [3]. Its absorptivity properties are due to their high surface area, a microporous structure and a high degree of surface reactivity. The removal efficiency is influenced by various factors, such as solution concentration, solution pH, ionic strength, and nature of adsorbate, adsorbent modification procedure, physical properties (surface area, porosity) and the chemical nature of activated carbon [4].

Moringa oleifera is the most widespread species plant family *Moringaceae*. *Moringa oleifera* is a multi-purpose tree whose seeds can be used as a coagulant in water treatment. Research has shown that the seed pod (husk) can be converted into activated carbon by carbonization and activation process. (Mcconnachie et al., [5] and Warhust et. al., [6]. There are a few methods in preparing of activated carbons from biomass, mainly being chemical activation techniques and physical activation. In this studies, the production of activated carbons was carried out using chemical activation method. Chemical activation is carried out by impregnated of chemical agent on the raw materials followed by pyrolysis in an inert atmosphere at high temperature. Chemical activation of activated carbon has been reported as more advantageous over physical activation due to higher yields, more surface area and better development of porous structures in carbon.

EXPERIMENTAL DETILES

Raw Materials

The *Moringa oleifera* seed pod was obtained as a waste from bioflocculant (another study by us). The dried coat was grinded with electrical blender and sieved with 1 mm sieve.

Proximate Analysis

The proximate analysis of *Moringa Oleifera* seed pod was conducted according to ASTM D 4442 for moisture content. ASTM E1755-01, Laboratory Analytical Procedure (LAP) NREL/TP-510-42622 for ash/inorganic content. ASTM E1690, Laboratory Analytical Procedure (LAP) NREL/TP-510-42619) for extractives content. TAPPI T203 cm-74 for holocellulose, hemicellulose and cellulose content. The carbon, hydrogen, nitrogen, and oxygen content were measured using a CHNS/O analyzer (Thermo Finnigan Model Eager 300).

Chemical Activation

Chemical activation method using zinc chloride ($ZnCl_2$) and sulfuric acid (H_2SO_4) were used to activate the raw material with ratio (1:10). 60 g of raw material was weight and impregnated in 600 ml 10% H_2SO_4 (v/v) and 10% $ZnCl_2$ (w/v), respectively for 24 hour with continuous stirring. The sample was heated until evaporated and continue dried in the oven at 100^{0}C, cooled, grind and sieve (1 mm). The sample was kept in the desiccator for further used.

Carbonization and Activation Process

The carbonization was performed in a tubular electrical furnace. The impregnated sample were place in alumina boat and inserted into the middle of furnace. The carbonization (T = 400^{0}C, 20 min) and activation were carried out at 600^{0}C and 800^{0}C (30 min) under N_2 (150 – 200 cm^3/min) with heating rate 10^{0}C/min. The activated carbon were washed with distilled water until the filtrate reached approximately pH 6 – 7. Sample was dried in the oven at 90 - 100^{0}C, cooled, grind, sieved (1 mm) and stored in the desiccator until used.

Activated Carbon Characterization

Brunaeur-Emmett-Teller (BET) surface analysis (ASTM D3663 – 03).

The BET surface area, external surface area, total pore volume and the pore size of the samples were determine by using BET equation and Quantachrome Nova Win2 (c), 1994 – 2002.

Thermal Gravimetric Analysis (TGA) (ASTM E1755 – 01)

Thermogravimetric analysis of plant biomass and AC samples were performed using thermogravimetric analyzer Perkin-Elmer TGA 7. The samples were heated from 30 - 900^{0}C

Scanning Electron Microscopy (SEM)

Scanning electron microcopy (SEM) analysis for plant biomass and AC samples were carried out at HV value of 10 kV and magnification of 500, 1000 and 8000x. The samples were first coated with conducting materials (chromium).

FTIR Spectroscopy

The FTIR spectrophotometry was carried out using Perkin Elmer Frontier instrument with scanning range 4000 – 400 cm$^{-1.}$

CHN Analysis

The CHN content was analyzed using Thermo Finnigan model Eager 300 analyzer. The percentage of oxygen was calculated by subtracting the C, H, and N from 100%.

Adsorption Experiments

Methylene Blue Assay

AC was tested to determine its capacity for removal of adsorbate from aqueous solution. In each experiment, 0, 0.1, 0.175, 0.25 and 0.5 g of AC3 were place in 150 ml flask containing 100 ml of 2 x 10^{-3} M of methylene blue (MB) adsorbate (pH 7). The flasks were placed in incubator shaker at 25^{0}C at shaker speed of 200 rpm. The sample mixture were taken at pre-set time interval (15 minutes) and their concentration were determined. Concentration of all samples was filtered before they were measured by UV-Vis Spectrophotometer HACH UV-Spectrophotometer DR5000 at λ = 668 nm.

4-chlorophenol TOC

In a conventional batch adsorption experiments, 0, 0.1, 0.175, 0.25 and 0.5 g of AC3 were place in 250 ml Erlenmeyer flasks containing 100 ml ppm of 4-chlorophenol (PCP) adsorbate (pH 7). The flasks were placed on an isothermal shaker at 30^{0}C at shaker speed of 200 rpm until equilibrium was attained. The resulting mixture was filtered and the filtrate was collected. The percentage PCP of removal was determined by UV-Vis Spectrophotometer at λ = 281 nm. The quantity of PCP in filtrate was determined by Total Organic Content (TOC) analyzer (680^{0}C, pressure= 200 kPa).

2. RESULTS AND DISCUSSION

Table 1 summarized the results for proximate analysis of *Moringa oleifera* seed pod (S2). CHN analysis revealed that the S2 contains mostly hydrocarbons (C, H and O) from carbohydrates with small amount of theoretical proteins.

Table 1: The summary of proximate analysis of *Moringa oleifera* seed pod (S2).

Parameters		Content (%)
Moisture content (%)		13.10 ± 1.07
Ash content (%)		28.62 ± 1.70
Extractives content (%		12.28 ± 0.30
Holocellulose (%)		46.00 ± 0.69
Cellulose (%)		28.66 ± 0.50
Hemicellullose (%)		17.34 ± 0.19
Elemental analysis		
	C	46.12
	H	6.73
	N	2.47
	O	44.68
Protein (%)		15.44

S2 was converted to activated carbon using zinc chloride and sulphuric acid as activating agent. These chemicals are common activating agents in activated carbon manufacturing industries which influence pyrolytic decomposition and inhibit tar formation. The carbonization process is to enrich the carbon content and create initial porosity and the activation process helps in enhancing the pore structure. Carbonization process take place at 400^{0}C for 20 minutes. During carbonization, primary carbonization gases are produces which can be categorized as permanent gases and oil (tar). The residue of the carbonization process is primary charcoal which serves as base materials for the activation step [6]. The charcoal the activated in the furnace at 600^{0}C or 800^{0}C for 30 minutes. Some of the carbon is oxidized which leads to the generation of pores.

After activation, the ACs produced were washed with water several times until activating agnet are completely remove (pH 6 – 7). This stage is important because during impregnation the activating agent will penetrated into raw materials particles and occupied substantial volume. Once they were extracted by intense washing, a large amount of porosity was created.

The percentage yields for ACs were summarized in **Table 2**. For AC1 and AC2 impregnated with H_2SO_4, the activation temperature at 600^{0}C and 800^{0}C did not affect much on the percentage of yields with the different only 3%. While, for AC3 and AC4 impregnated with $ZnCl_2$, the carbonization temperature at 800^{0}C compare to 600^{0}C reduce the percentage of yields from 68.4% to 34.4%. AC impregnated with $ZnCl_2$ gave higher yields compared to H_2SO_4 at both studied temperatures.

Table 2: Percentage of different activated carbons from *Moringa oleifera* seed pod.

Yields (%)	Activated Carbons			
	AC1	**AC2**	**AC3**	**AC4**
Replicate 1	15.5	13.5	33.9	56.0
Replicate 2	17.3	13.9	32.8	79.1
Replicate 3	17.3	13.8	36.3	70.0
Average	16.7 ± 1.0	13.7 ± 0.2	34.4 ± 1.8	68.4 ± 11.6

Table 3 – 4 summarized the thermal stability and BET analysis of *Moringa oleifera* (S2) and AC (AC1 – AC3) samples. The TGA curves for S2 sample show two stages of weight loss in the region of 30 – 900^{0}C (**Figure 1–2**). The

first stage at around 60 – 140^{0}C (stage 1) was due to the removal of water within the biomass. Meanwhile, a wide range of weight loss at around 250 - 450^{0}C (stage 2) was due to degradation process of lignocellulosic materials (decomposition of glycosyl units of cellulose or lignin) followed by the formation of char. For AC samples, it was observed that the temperature at 50% weight loss, $T_{50\%}$ were high as compared to S2 samples. This could be due to higher content of char (activated carbon), which exhibit higher thermal stability. It is interesting to point out at 550^{0}C (W_{550^0}), the weight loss for AC samples were higher to that of S2, could due to the high purity of char material.

Table 3: TGA data obtained for the samples.

Samples	TGA analysis		
	$T_{i,\ onset}$ (^{0}C)	$T_{50\%}$ (^{0}C)	W_{550^0} (^{0}C)
S2	146	350	30
AC1	489	-	87
AC2	600	-	80
AC3	610	-	90

Table 4: BET data obtained for the samples.

Samples	BET analysis			
	S_{BET} (m^2g^{-1})	S_{ext} (m^2g^{-1})	V_{pore} (cm^3g^{-1})	D_{pore} (nm)
S2	2.45	4.42	0.0018	3.13
AC1	N/A	N/A	N/A	N/A
AC2	524.83	467.79	0.0214	1.67
AC3	853.68	414.23	0.1806	2.13

On the most important features of adsorbents is their surface area and porosity. The BET surface area, total pore volume and average pore diameter obtained for the *Moringa* (S2) was found to be 2.45 m^2g^{-1}, 0.0018 cm^3g^{-1} and 3.13 nm respectively, which is lower than all AC samples. After the pyrolysis treatment of *Moringa*, it can be seen that there was an improvement in the BET surface which connotes a good property of an adsorbent (due to the production of porous materials). Based on the average pore diameter (1.67 – 2.13 nm), the AC can be classified as microporous according to the International Union of Pure and Applied Chemistry (IUPAC) [8] which classified as micropores (<2 nm diameter), mesopores (2 – 50 nm diameter) and macropores (>50 nm diameter).

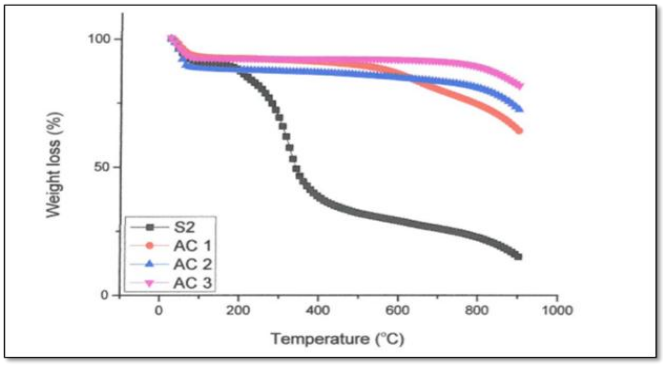

Figure 1: The TG curves of *Moringa oleifera* seed pod and activated carbons.

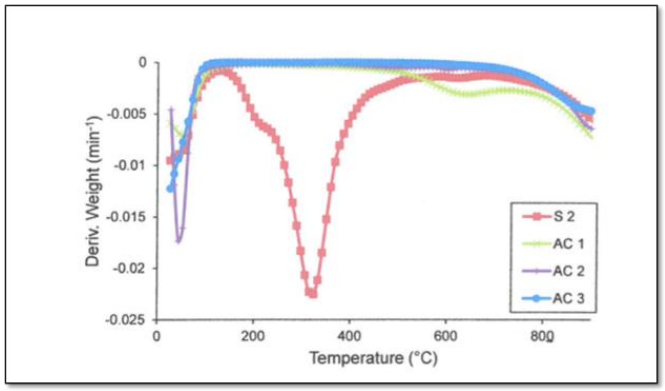

Figure 2: The DTG curves of *Moringa oleifera* seed pod and activated carbons.

The morphology of *Moringa* and activated carbon samples was investigated using SEM. Scanning electron micrographs show changes in the morphology of the materials in terms of size and the formation of pores. It is worth noting, as seen in **Figure 4** – **6**, that the pyrolysis process has altered the morphology of activated carbon samples compared to *Moringa* (S2). **Figure 3** shows a smooth fiber surface with tangled like structure of OPF biomass, while **Figure 5** – **6**, shows formation of honeycomb-like pores, which are often aggregated, and a rough surface morphology of AC samples. It was also observed that AC1, didn't show any formation of pore or maybe very small (**Figure 4**), which justify the reason why we cannot get any data for BET results.

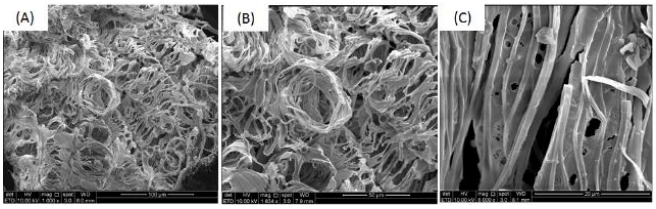

Figure 3: SEM images of *Moringa oleifere* seed pod (S2) at the magnification of (A) 500x, (B) 1000x, and (C) 8000x.

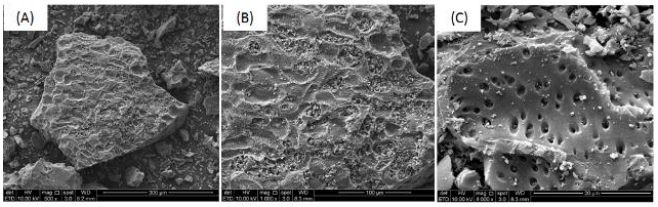

Figure 4: SEM images of activated carbon, AC1 at the magnification of (A) 500x, (B) 1000x, and (C) 8000x.

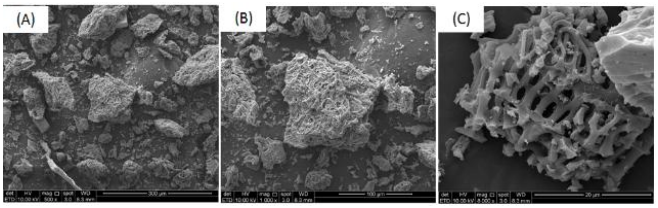

Figure 5: SEM images of activated carbon, AC2 at the magnification of (A) 500x, (B) 1000x, and (C) 8000x.

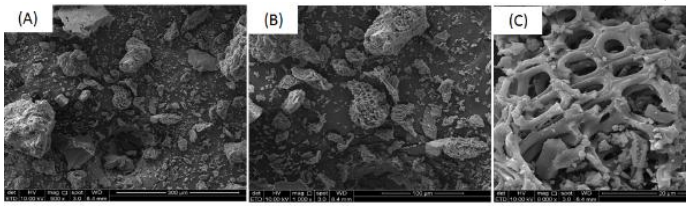

Figure 6: SEM images of activated carbon, AC3 at the magnification of (A) 500x, (B) 1000x, and (C) 8000x.

Table 5 summarized result for elemental analysis of AC2 and AC3. This results clearly revealed that both AC have very high carbon content, which justify the purity of the prepared AC. Small trace of hydrogen and nitrogen elements were detected, which corresponds to herbaceous impurities.

Table 5: Elemental analysis of AC2 and AC3

Elemental analysis (%)	AC2	AC3
Carbon (C)	69.25	68.25
Hydrogen (H)	1.32	1.42
Nitrogen (N)	1.94	2.01
Oxygen (O)	27.49	28.32

FTIR spectroscopy of AC2 and AC3 are shown in **Figure 7**. The FTIR spectra show similar trends to that of previous findings by many authors and have five major's absorption bands at 3413 – 3415 cm^{-1}, 2015 – 2017 cm^{-1}, 1618 – 1621 cm^{-1}, 1073 – 1123 cm^{-1}, and 482 – 616 cm^{-1}. The band at about 3415 cm^{-1} is attributed to O-H (stretching) and can be assigned to O-H vibrations, suggesting the presence of phenolic groups of cellulose and lignin. The band at 2016 cm^{-1} is typically is attributed to alkyne group. The appearance of bands at 1618 and 1074 cm^{-1} indicate the presence of C=C stretching for unsaturated aliphatic structures and alcoholic group respectively. While, band at 482 – 616 cm^{-1} related to the long chain band. Treating biomass with oxidizing agents (H_2SO_4 and $ZnCl_2$), introduce the surface of activated carbon with oxygen functional group. It can be conclude that, surface functional group were significantly similar between sample treated with H_2SO_4 and $ZnCl_2$.

From the result of AC characterizations, AC3 was found to be the best AC. AC3 was further undergo adsorption analysis using two adsorbates methylene blue and PCP. The adsorption curves are single, smooth and continuous until t = 120 min. it was found that AC3 at 0.5 g gave the best MB removal compared to others. 90.7% of removal after 30 minutes of contact.

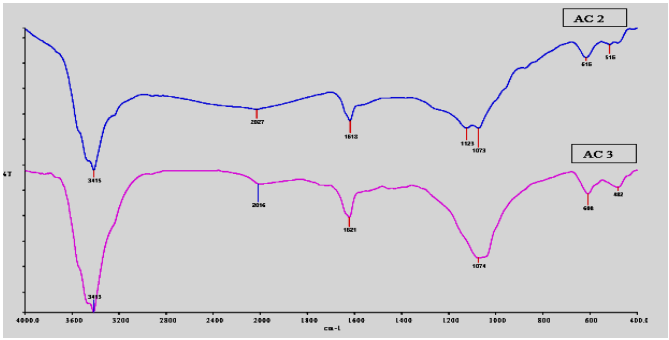

Figure 7: FTIR spectra for AC2 and AC3

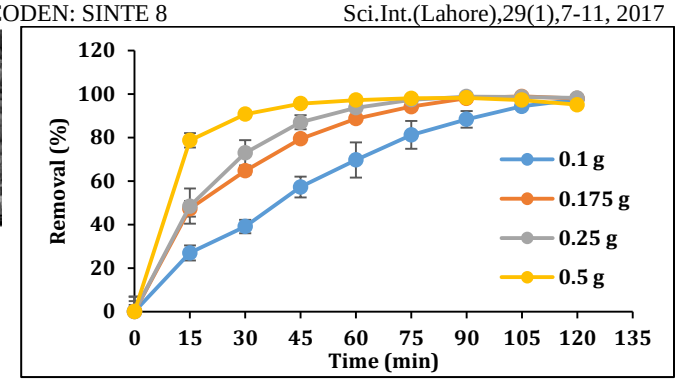

Figure 8: Effect of contact time and mass of AC3 on absorption of MB on AC3 (Initial concentration = 2 x 10^{-3} M, pH = 7, absorbent dose = 0.1 – 0.5 g per 100 ml solution, agitation rate = 200 rpm and temperature = 25^{0}C.

In the PCP adsorption studies, it was revealed that as the amount of AC3 increased, the percentage of PCP removal was increased (**Table 6**). The highest removal at AC3 = 0.5 g, 96.03%. Additionally, the TOC show similar trends to that UV absorbance where 0.5 g of AC3 = 0.5 g gives lowest TOC value, 1.735 ppm (97.4% reduction) as compared to untreated PCP sample.

Table 6: Absorbance and TOC values of PCP samples treated with AC3.

Weight of AC3 in PCP (g)	UV-Vis		TOC	
	Abs. (A)	Removal (%)	Conc. (ppm)	Removal (%)
Blank	1.310		66.95	
0.10	0.129	90.15	7.728	88.5
0.175	0.069	94.73	3.334	95.0
0.25	0.056	95.73	1.908	97.1
0.50	0.052	96.03	1.735	97.4

3. CONCLUSIONS

Activation time and type of chemical activating agent were important parameter affecting the production of activated carbon from *Moringa oleifera* seed pod. Temperature at 800^{0}C gave better properties compare to 600^{0}C. Activated carbon impregnated with $ZnCl_2$ gave better BET value, 853.68 m^2g^{-1} compare to H_2SO_4, 524.83 m^2g^{-1}. Adsorption experiment showed that AC3 able to remove 90.7 % of methylene blue solution (2 x 10^{-3} M) and 97.4% of 4-chlorophenol (66.95 ppm), respectively. Finding showed that *Moringa oleifera* seed pod has the potential to be a promising precursor for the production of activated carbon.

5. REFERANCE

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