

Enhancement of CO₂ Adsorption on Activated Carbon Prepared from *Canarium ovatum* Engl. Nut Shells

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New sources of activated carbon (AC) are desired for CO₂ capture. This study explored the potential of Philippine indigenous Pili tree (*Canarium ovatum* Engl.) waste nut shell as a source of new activated carbon. The charred sample has high fixed carbon content (86.81%), which upon activation, showed higher surface area (701 m²/g) and larger pore volume (0.45 cm³/g) compared to the unactivated sample. Modification of the carbon surface through impregnation of different amines resulted in lower surface areas, narrower pore volumes, and changes in morphology (from uniform geometric shape to spongy microstructures). The amine modified samples gave slight decrease in X-ray diffraction interlayer spacing ($d_{(002)}$) resulting in formation of micro crystallites that may promote CO₂ adsorption. Indeed, the modified AC samples had higher adsorption capacities for CO₂ than the original AC. The amount of adsorbed CO₂ on pentaethylenhexamine-modified AC was up to 2.380 mmol/g at 1 atm and 293 K, a 173% increase in comparison with that of the original AC.

Key words: Activated Carbon, *Canarium ovatum*, CO₂ Capture, CO₂ Adsorption, Materials science, Pili nut

INTRODUCTION

The world is in search for technologies designed to reduce greenhouse gas emissions. Among the greenhouse gases, the gradual increase in the atmospheric concentration of carbon dioxide (CO₂) due to burning of fossil fuel is very alarming (Boden et al. 2012). The most realistic short term technology, albeit a costly process, on the capture and sequestration of post-combustion CO₂ is achieved by amine scrubbing of industrial flue gases (Rao & Rubin 2002). Several technologies for post-combustion CO₂ capture (Figuerola et al. 2008) such as liquid solvent absorption (Chaffee et al. 2007), cryogenic techniques

(Tuinier et al. 2011), membrane separation (Ahmad et al. 2010), solid sorbents (Siriwardane et al. 2001), and pressure (and/or temperature) swing adsorption (Plaza et al. 2011) are being studied. Adsorption technologies offer potential advantages over amine scrubbing because their low energy requirement, cost advantage, and ease of applicability over a relatively wide range of temperatures and pressures. However, the success of this approach is dependent on the development of easily regenerable and durable adsorbents with a high CO₂ selectivity and adsorption capacity. Among the materials being studied, zeolites have shown promising results for separating CO₂ from gas mixtures but the presence of water inhibits their CO₂ adsorption capacity (Brandani & Ruthven 2004).

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Aside from the size and charge density, the adsorption efficiencies of zeolites are largely affected by the chemical composition of cations in their porous structures. As a result, CO₂ adsorption capacity greatly declines in the presence of moisture because of the enhanced hydrophilic character owing to the presence of cationic species (Wang et al. 2011). Activated carbons, which are cheap, insensitive to moisture due to the absence of inorganic cations, and can easily be regenerated are potential candidates for CO₂ capture because their adsorption capacities at ambient pressure are high. The adsorption capacities of activated carbons are governed by the surface chemistry on the carbon. Hence, surface modification by introducing nitrogen functionalities (Lewis base) on the carbon surface enhances the CO₂ (weak Lewis acid) adsorption capacity (Plaza et al. 2007, Przepiórski et al. 2004, Zhang et al. 2010, Gray et al. 2008, Arenillas et al. 2005).

In this work, a novel source of activated carbon and its subsequent surface modification with amine groups was described for CO₂ capture. The new precursor for activated carbon was derived from the Pili tree (*Canarium ovatum* Engl.), a hardy rainforest tree indigenous to the Philippines (Figure 1). The tree bears an edible nut which is protected in a thick and very hard pointed shell, covered in turn with a thick black skin when ripe. The Pili nut shell that houses the single, sweet kernel is slender with a length and diameter of approximately 2½ inches and ¾ inches,

respectively (Coronel 1991; Quisumbing 1978). The Pili nut shell, being a waste material in Pili nut processing has not been fully studied (Pondevida 2011); hence, this study explored the potential of activated carbon from the waste Pili nut shell as an efficient adsorbent material for CO₂ capture.

MATERIALS & METHODS

All chemicals used were procured from Aldrich with 99% purity. The waste shells of Pili nut from the Bicol Region in the Philippines were utilized as carbon precursor for activated carbon. The shells were crushed, washed, and dried affording brown, flat, and irregularly shaped particles (30 g, 2.00-4.00mm size). The shells were packed (in air) to full capacity into a steel vessel and tightly closed for carbonization process. Carbonization was carried out at 400°C in a closed steel vessel placed in a muffle furnace for 30 minutes. The charred material was ground (ball miller) and sieved through a 200 mesh sieve (74 microns) to obtain a fine powder with an average char yield of 22%. The resulting fine carbon material was designated as Pili nut shell char (PSC).

The PSC was activated under N₂ atmosphere in a quartz container, via chemical activation, using NaOH in two weight ratios of carbon:OH⁻ (8:1 and 4:1), and fired in a tubular furnace at 750°C for 1 hour. The cooled sample was washed with HCl (5M) and filtered and washed with



Figure 1. Pili (*Canarium ovatum* Engl.) tree, ripened fruit and nut shell.

hot distilled water (80°C) until the filtrate was free of chloride ions. The sample was dried in an oven at 120°C for 24 hours. The material obtained was designated as Pili nut shell activated carbon (PSAC).

The PSAC was subjected to surface modification by oxidizing the carbon surface with HNO₃ (10M) in ratio of 1:80 (1g C: 80g HNO₃). The mixture was refluxed at 90°C for 1h, cooled and washed with de-ionized water to pH 7, and finally oven-dried. The same procedure was done for PSC for comparison. The samples were designated as PSAC_a and PSC_a, respectively. These samples were then subjected to surface amination in a two-neck round bottom flask under N₂ atmosphere using toluene (1:40, carbon:toluene) as solvent. Thionyl chloride (1:2, carbon:SOCl₂) was first added with constant stirring at 50°C for 12 hours then washed extensively with toluene and vacuumed three times. The acyl chloride of carbon was mixed with 40 ml of toluene and reacted with liquid amine triethylenetetramine **1** (TETA; N content = 29.58 wt%; Aldrich 99%) in 1:4 carbon:amine ratio. The reaction was maintained at 50°C for 1h. The amine-functionalized carbons were washed with ethanol several times to ensure the removal of all free chemicals from the carbon and dried under vacuum. The obtained sample was oven-dried at 110°C for 24 hours to give a black powder designated as PSAC-1. The same procedure was done for liquid amines pentaethylenehexamine **2** (PEHA; N content = 36.15 wt%; Aldrich 99%) and polyethyleneimine **3** (PEI; M_n = 600; N content = 33.97 wt%; Aldrich 99%) to obtain PSAC-2 and PSAC-3, respectively. The amine-modified PSCs were designated as PSC-1, PSC-2, and PSC-3.

Chemical characterization of the samples involved standard procedure for proximate analysis, moisture (ASTM D3173-03), ash (ASTM D3174-04), and volatile combustible matter (ASTM D3175-07). FT-IR was recorded on JASCO 4200 spectrometer using KBr pellet method. The Boehm titration was done by subjecting the samples (200mg) to 25mL of 0.05M solution of reaction bases (NaOH, Na₂CO₃ and NaHCO₃) under constant stirring (30 rpm) for 24 hours. After filtering the mixture, a 10 mL aliquot was titrated with 0.05M HCl to the desired pH. Sample characterizations involved X-ray Diffraction (XRD) (XRD analyzer with diffractometer operated at 40kV and 30mA using CuK α radiation at a scan rate of 2°/min), Scanning electron microscopy SEM (JEOL JSM instrument at 10.0 kV with gold coating), and Elemental analysis (CHN elemental analyzer, Perkin Elmer 2400). The nitrogen sorption and carbon dioxide sorption studies were carried out on Micrometrics ASAP 2010 system at -196°C for N₂ sorption and Micrometrics ASAP 2020 system at 25°C for CO₂ sorption. Prior to analysis, carbon samples were out-gassed at 100°C under vacuum for 24 hours. The apparent surface areas (S_{BET})

were calculated from the physical adsorption of N₂ using the BET equation in the linear form and the total pore volumes (V_p) were evaluated using Gurvitch's rule ($p/p^0 = 0.99$). The average pore width (D) of the adsorbents was estimated by means of the expression $4V/S_{BET}$. The micropore volumes (W₀) were calculated by the Dubinin-Radushkevich (DR) method ($W = W_0 \exp[-k(e/\beta)^2]$); where, W/W₀ is the fraction adsorption space filled at relative pressure P/P₀) from CO₂ adsorption isotherms (assuming an affinity coefficient of 0.36).

RESULTS AND DISCUSSION

Proximate analysis (Table 1) of the samples showed the raw biomass (PS) containing lower ash content but higher moisture and volatile matter compared to the carbonized material (PSC). The ultimate analysis was carried out theoretically from the proximate analysis data (Sanger et al. 2011). The ultimate carbon content of PS (62.8%) is higher compared to the previously studied nut shells (Heschel & Klose 1995) like coconut, which is the common source of activated carbon indicating that the Pili nut shell is a highly lignocellulosic material. After carbonization, the char showed a substantially high carbon content of 89.02% indicating a suitable precursor for activated carbon production.

Activation process

The activation of PSC with NaOH influences pyrolytic decomposition where NaOH acts as dehydrating agent,

Table 1. Proximate and ultimate analyses of Pili (*Canarium ovatum* Engl.) nut shell samples.

Sample	Proximate Analysis (% dry basis)				
	Ash	M ^a	VM ^a	FC ^a	C ^b
Pili Shell (PS)	1.6	7.2	80.7	10.5	62.8
Pili Shell Char (PSC)	4.6	0.7	7.9	86.8	89.0
Walnut ^c	8.2	1.5	--	--	50.5
Hazelnut ^c	8.7	1.2	--	--	51.9
Coconut ^c	11.2	1.2	--	--	52.7
Brazil nut ^c	11.8	1.8	--	--	54.4
Almond ^c	8.5	2.0	--	--	51.1
Pistachio ^c	6.5	1.9	--	--	47.3
Peanut ^c	6.8	2.2	--	--	49.9

^aM: Moisture; VM: volatile matter; FC: fixed carbon, calculated by difference

^bUltimate carbon content calculated theoretically from the proximate analysis data

^cData derived from Heschel W, Klose E, 1995

etching and swelling the surface, inhibiting the formation of tar, and enhancing the yield of carbon (Tseng 2007). The obtained material was designated as Pili nut shell activated carbon (PSAC). The elemental analysis of the PSC and PSAC (Table 2) showed that the charred material (PSC) contains 27.92% O confirming that it already contains oxygen functional group. Upon activation with NaOH, the PSAC generated showed a slight increase in carbon content and a small decrease in oxygen content suggesting structural

Table 2. Elemental analyses of Pili (*Canarium ovatum* Engl.) nut shell samples.

Sample	Elemental Analysis ^a (wt %)			
	C	H	N	O
PSC	70.68	1.40	0.0	27.92
PSAC	74.58	0.23	0.0	25.19
PSCa	46.02	2.03	0.0	51.95
PSACa	71.76	0.28	0.0	27.96
PSC-1	49.55	2.61	6.63	41.21
PSAC-1	73.46	1.09	5.15	20.3
PSAC-2	51.56	1.18	8.09	39.22

^aElemental analysis obtained experimentally by CHN Elemental Analyzer.

changes in the activated carbon surface.

The surface of PSC, as revealed by FT-IR analysis (Table 3), is predominantly composed of C-O type groups present

Table 3. Summary of FTIR data.

PSC	C-O stretch (1300-1000 cm ⁻¹) ethers, acid and esters
PSAC	C=O stretch carboxyl type (1760-1690 cm ⁻¹) C=O stretch (1637cm ⁻¹) O-H stretch (3570-3200 cm ⁻¹)
PSCa	C=O stretch carboxyl type (1690-1760 cm ⁻¹)
PSACa	C=O stretch carboxyl type (1690-1760 cm ⁻¹) O-H stretch (3570-3200 cm ⁻¹)
PSC-1	N-H stretch (3700-3510 cm ⁻¹) C-N stretch (1360-1150 cm ⁻¹)
PSAC-1	N-H stretch (3700-3510 cm ⁻¹) C-N stretch (1360-1150 cm ⁻¹) O-C-N bend (641 cm ⁻¹) C-N stretch (1250-1150 cm ⁻¹)
PSAC-2	N-H stretch (3700-3510 cm ⁻¹) C-N stretch (1360-1150 cm ⁻¹) O-C-N bend (641 cm ⁻¹)

in ethers, acids, and esters (1000-1300cm⁻¹). Activation of the carbon material (PSAC) led to the oxidation of carbon surface and resulted in generation of C=O type carboxyl groups (1690-1760 cm⁻¹) and carbonyl groups (1637 cm⁻¹). The presence of broad band at 3570-3200, an O-H stretching vibration of surface hydroxyl groups, indicated the presence of hydrogen bonding interaction.

The change in surface functionalities upon activation is further confirmed by Boehm titration (Table 4) to detect acidic oxygen functionalities. Boehm titration determines the relative amounts of oxygen containing acidic groups on the activated carbon based on the fact: that NaOH neutralizes the carboxylic, phenolic, and lactone groups; Na₂CO₃ neutralizes carboxylic and lactone groups; and NaHCO₃ neutralizes only carboxylic groups (Boehm 1994). PSC was found to contain phenolic group, explaining the presence of oxygen. The Boehm titration result of PSAC showed that upon activation, disappearance of the phenolic functionality and formation of lactonic group can be observed. The change in surface chemistry showed that the basal plane has been modified upon activation with NaOH where the alkali influences the activation process resulting to functional group modification (Yamashita & Ouchi 1982). Changes in these peripheral functional groups

Table 4. Acidic functional group determination of different samples of Pili (*Canarium ovatum* Engl.) nut shells using Boehm titration.

Sample	Acidic Group (mmol/g)		
	Phenolic	Carboxylic	Lactonic
PSC	0.3567	0	0
PSAC	0	0	0.8570
PSCa	0.3798	0.1754	0
PSACa	0.9930	0.7103	0.7155

lead to a poorly packed and disordered graphene layers affecting the surface area and pore distribution of the material (Yoon et al. 2004).

Pore volume (V_{DR}) and surface area (S_{BET}) analyses (Table 5) of the samples activated with NaOH using density functional theory (DFT) method and using the nitrogen adsorption isotherm at -196°C, respectively, showed larger pore volume and higher surface area compared to that of the unactivated PSC samples with increasing influence as the ratio of activating agent (NaOH) increases. The observed increase in surface area can be attributed to the greater degree of graphitization as well as to the proposed disorder in the graphene layers as a result of changes of oxygen surface functional groups on the basal carbon.

Table 5. Pili (*Canarium ovatum* Engl.) nut shell carbonized (PSC) activation with NaOH at three different ratios.

Sample	Ratio (wt:wt, NaOH:C)	% Yield	Pore volume, V _{DR} (cm ³ /g)	Surface area, S _{BET} (m ² /g)
PSC unactivated	0:1	-	0.2050	327.45
PSAC (4:1)	4:1	49.5	0.4501	701.50
PSAC (8:1)	8:1	44.0	0.5451	817.19

Surface modification

Surface modification via acid-base treatment was demonstrated on the PSAC (4:1) sample and compared with PSC sample. Treating the PSAC and PSC samples with HNO₃ gave the PSACa and PSCa powders, respectively. Acid modification of the samples resulted to an increase in the C=O type stretching of carbonyl groups as shown in FT-IR analysis. Elemental analyses revealed (Table 2) a significant decrease in carbon content (from 70.68% to 46.02%) accompanied by an increase (from 27.92% to 51.95%) in oxygen content of the acid treated PSCa sample in comparison to the starting material (PSC). The results can be attributed to the generation of carboxylic acid in PSCa upon acidification process.

The change in surface chemistry is confirmed by Boehm titration of the acidified samples PSCa and PSACa (Table 4). The original PSC sample showed only phenolic groups and no carboxylic and lactonic groups. Upon acidification, small amount of carboxylic acid groups were formed along with the phenolic groups indicating a change in surface chemistry to afford a new material PSCa. The PSACa results, on the other hand, showed high amounts of phenolic, carboxylic, and lactonic groups. A slight decrease of the lactonic group compared to the original PSAC sample was also observed. For a typical activated carbon, regardless of activation method, the basal plane contains acidic and basic sites (Shafeeyan et al. 2010). The Boehm

titration result suggests that the formation of phenolic and carboxylic functional groups is a result of acid treatment and can be attributed to the presence of ether and ketone moieties on the carbon surfaces (Shafeeyan et al. 2010).

Amine functionalization

To increase the CO₂ adsorption capacity of the adsorbent material, the carbon surface was modified by wet impregnation of nitrogen groups to the basal plane of the activated carbon. Three different kinds of amines with increasing N percentage namely, triethylenetetramine (TETA) **1**, pentaethylenehexamine (PEHA) **2**, and polyethyleneimine (PEI) **3**, were used (Figure 2).

Treatment with thionyl chloride (SOCl₂) followed by reaction with the amines afforded the amine terminated carbon materials (Figure 3) namely PSC-1, PSC-2, PSC-3, PSAC-1, PSAC-2 and PSAC-3.

Photographic profiles of the products (Figure 4) revealed a black loose powder for PSC-1, PSAC-1 and PSAC-2 and a lump clay-like material that cannot be pulverized despite extensive air and oven drying was observed for PSC-2, PSC-3 and PSAC-3. A powder form is necessary in adsorption experiments; hence, further characterization and experiments were not done on the latter samples.

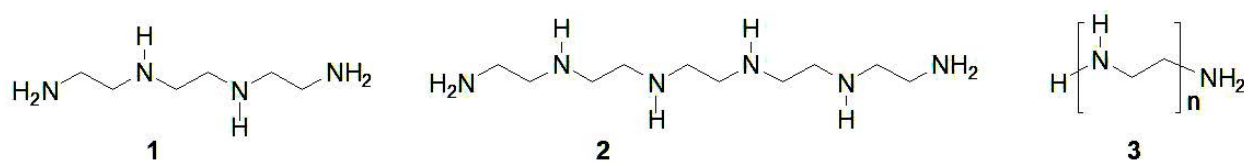


Figure 2. Molecular structures of TETA (**1**), PEHA (**2**), and PEI (**3**).

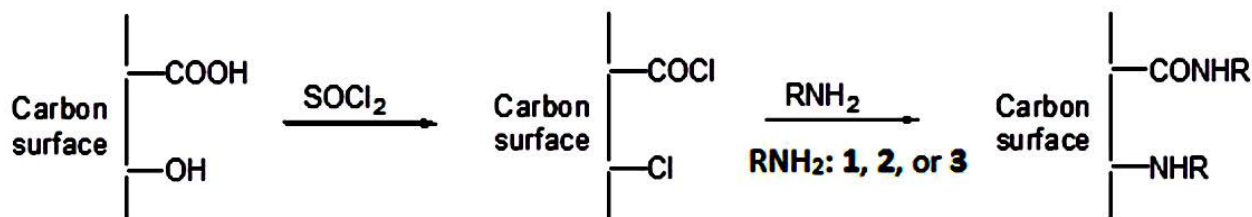


Figure 3. Schematic representation of the amination of Pili (*Canarium ovatum* Engl.) nut shell activated carbon.

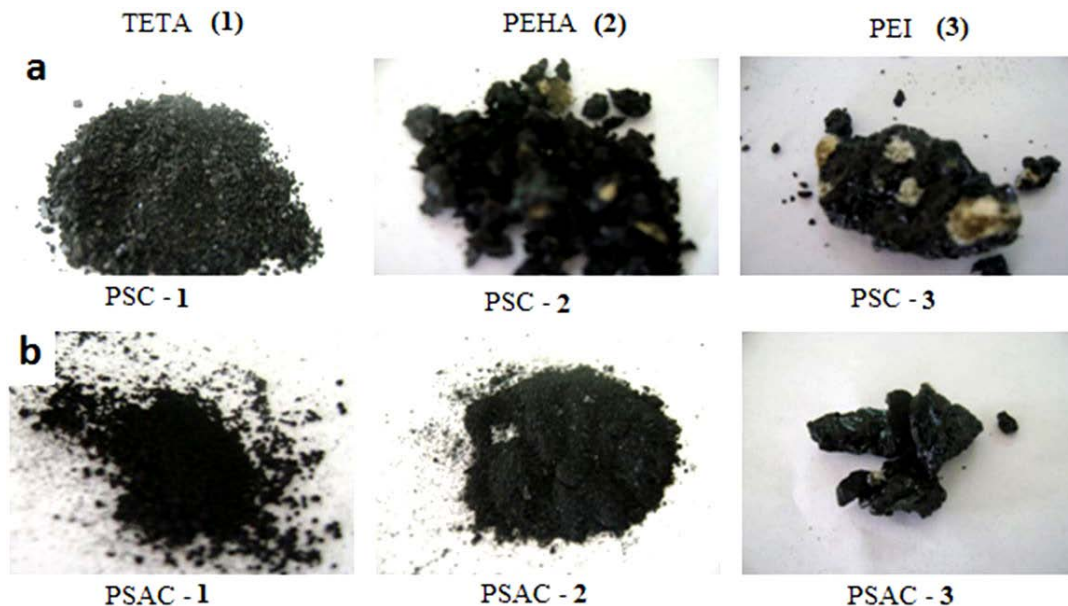


Figure 4. Photograph of samples treated with 3 kinds of amine [TETA (1), PEHA (2), and PEI (3)] a) Pili (*Canarium ovatum* Engl.) nut shell carbonized (PSC), b) Pili nut shell activated carbon.

Elemental analysis (Table 2) of the amine treated samples PSC-1, PSAC-1, PSAC-2 showed an increase in nitrogen content from 0% to 6.63%, 5.15%, and 8.04%, respectively, attributed to additional nitrogen groups incorporated to the samples.

FT-IR analysis (Table 3) of the amine functionalized samples generated the N-H (3700- 3510cm⁻¹) and C-N

(1360-1150 cm⁻¹) type groups. Moreover, amide formation can be deduced from the peak found at 641 cm⁻¹ indicative of OCN bending. A broad peak at 1250-1150 cm⁻¹ was also present indicating C-N stretching in secondary, tertiary, or aromatic ring. The FT-IR results showed the impregnation of amine groups on the carbon network.

The structural parameters and features of PSAC and

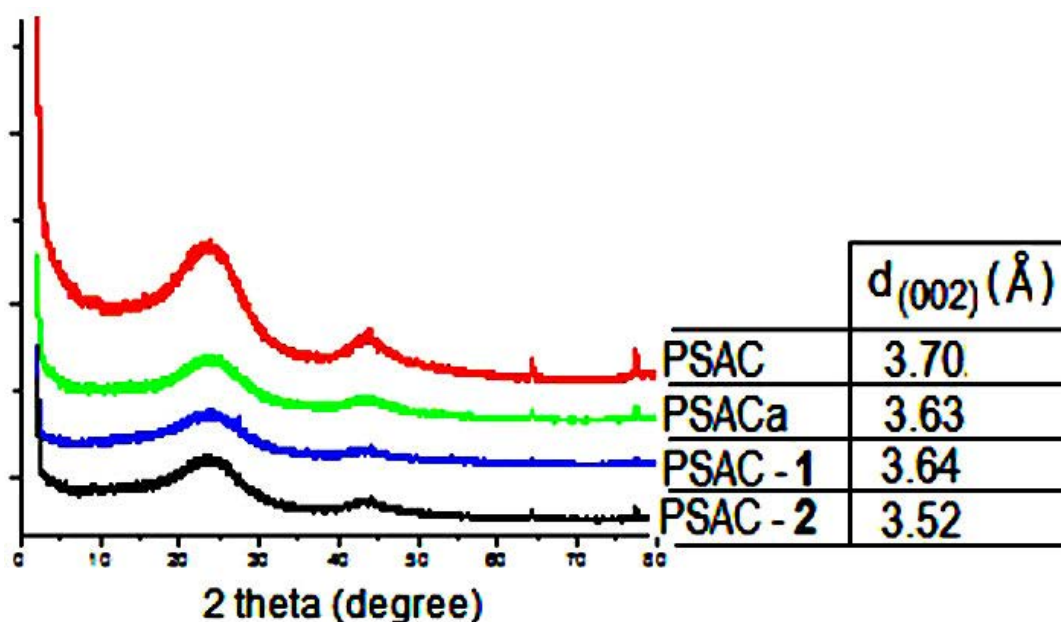


Figure 5. Powder X-ray diffraction patterns and crystallographic parameter of Pili (*Canarium ovatum* Engl.) nut shell activated carbon (PSAC) samples.

its resulting derivatives were obtained from the X-ray Diffraction (XRD) analysis. The XRD curves of PSAC samples (Figure 5) exhibited two broad peaks at 2θ values 24° and 43° which correspond to the peaks of graphite (Lua & Yang 2004). The crystallographic parameter of the PSAC samples (range of interlayer spacing $d_{(002)}$ 3.52 – 3.70 Å) was found to be greater than that of the $d_{(002)}$ values of graphite (3.35 Å), indicating that the structure of the PSAC samples is turbostratic (intermediate structures between graphite and amorphous state) or random layer lattice structure (Zondlo 2004). The parameter $d_{(002)}$ is a measure of the perfection in the stacking structure periodicity. Amine modification of PSAC samples gave a slight decrease in interlayer spacing ($d_{(002)}$) indicating that the graphitic layers connect to each other more closely with the help of the amines creating small size crystallites

that may promote high CO₂ adsorption.

The surface morphology of the samples as determined by scanning electron microscopy (SEM) show notable differences upon acid-base treatment. The PSAC sample (Figure 6a) showed a uniform geometrical surface, which upon acidification (Fig. 6b) turned into a smoother layer indicating structural change. Modification of PSAC with TETA (Fig 6c) and PEHA (Fig. 6d) showed dramatic changes in surface morphology: it becomes spongy and more amorphous indicative of changes in surface area. The same surface morphological changes can be observed in PSC (Figure 7) from polygonal pattern (a), to formation of microstructures (b), to spongy surface (c) upon amine modification.

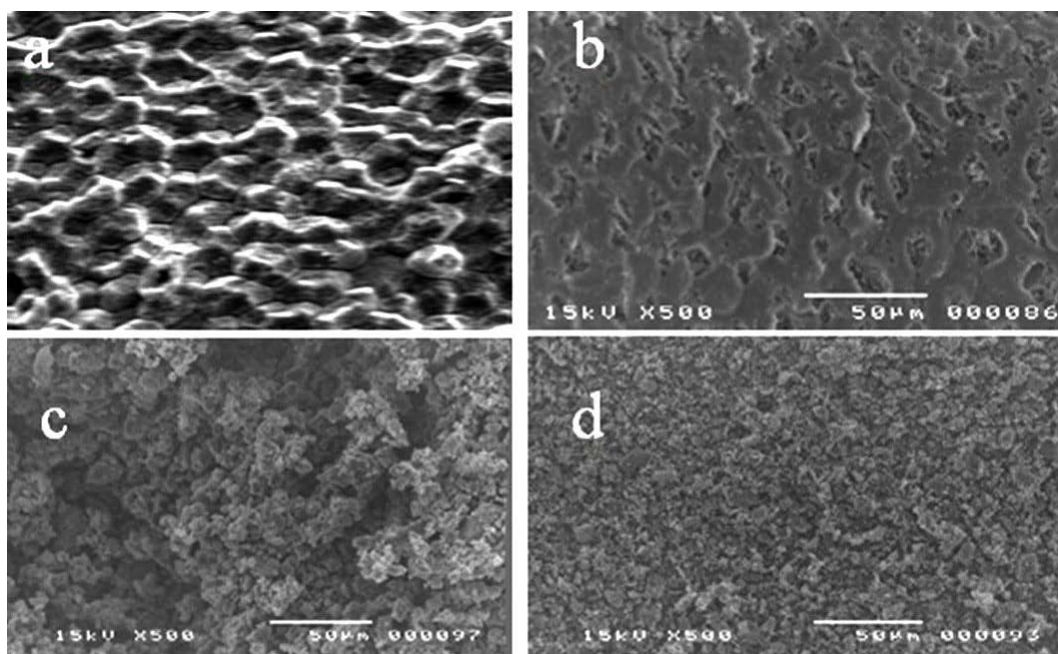


Figure 6. SEM micrograph of PSAC samples a) Pili nut shell activated carbon (PSAC) b) acidified Pili nut shell activated carbon (PSACa) c) triethylene tetramine treated Pili nut shell activated carbon (PSAC-1) d) pentaethylenehexamine treated Pili nut shell activated carbon (PSAC-2).

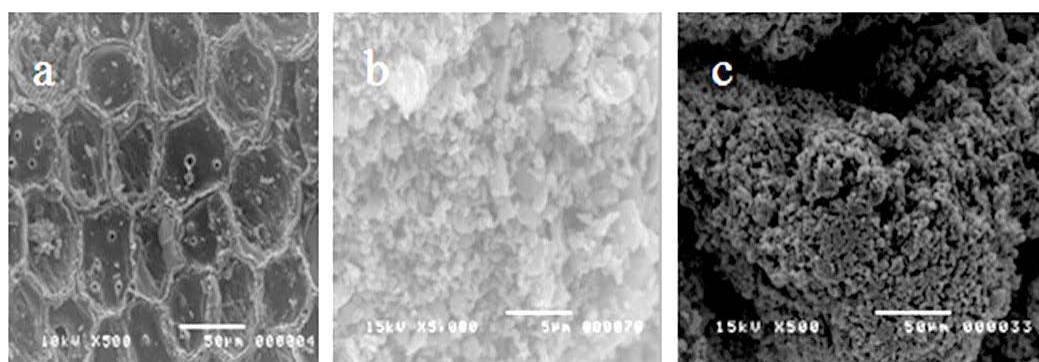


Figure 7. SEM micrograph of PSC samples a) Pili nut shell carbonized (PSC) b) acidified Pili nut shell carbonized, (PSCa) c) triethylene tetramine treated Pili nut shell carbonized (PSAC-1).

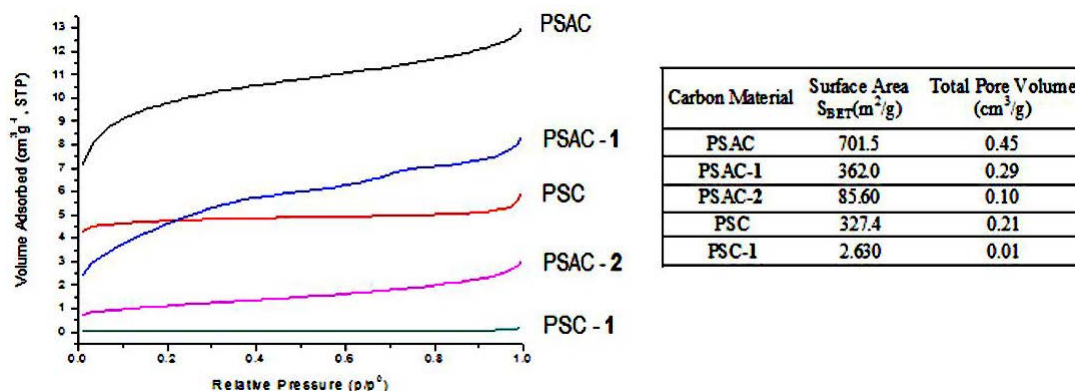


Figure 8. Nitrogen adsorption isotherms at -196°C and textural characteristics of the sorbents.

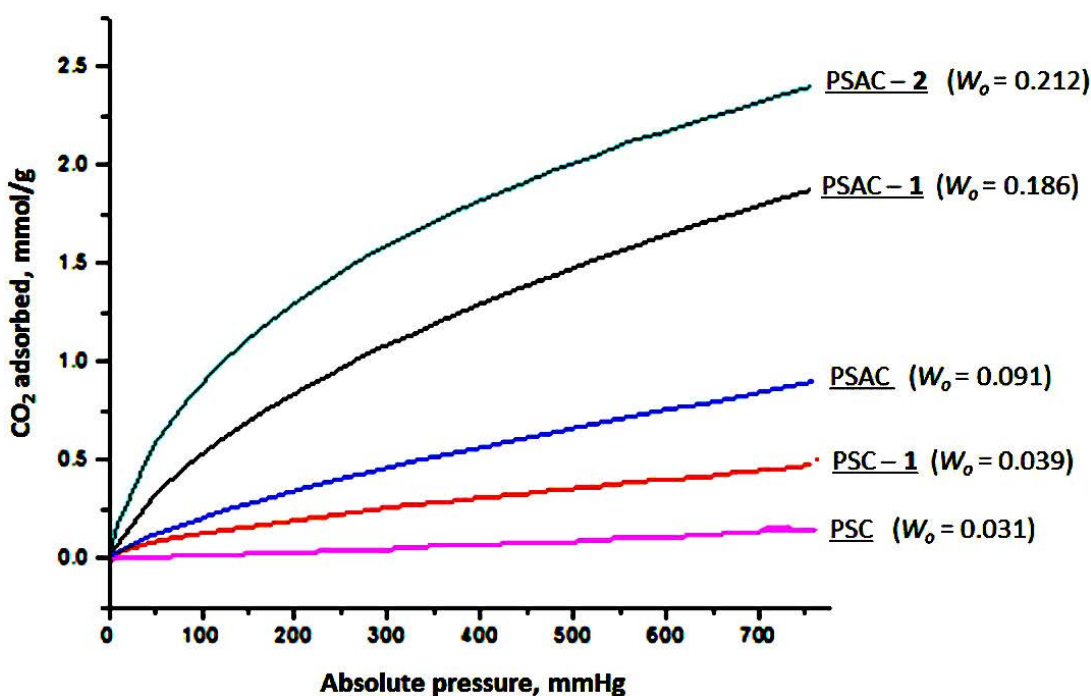


Figure 9. Carbon dioxide isotherms at 25°C of Pili (*Canarium ovatum* Engl.) shell samples. Figure in parentheses: Narrow Micropore Volume W_0 (cm^3/g).

Nitrogen and Carbon dioxide sorption analysis

The textural properties of the sorbents were determined by the adsorption of N₂ at -196°C and CO₂ at 25°C. The N₂ adsorption isotherms of the Pili nut shell samples (Figure 8) show type I isotherms characteristic of microporous materials. Isotherm of PSAC sample shows a more open knee at low relative pressure, indicating a broader pore size distribution with larger pore size. Between the PSC and PSAC isotherms, the amount of the adsorbed nitrogen in PSAC sample is higher; thus, the activation with NaOH substantially develops the surface morphology of the starting char and its capacity to adsorb N₂.

The textural parameters calculated from the N₂ and CO₂ adsorption isotherms show that PSAC sample gave significant reduction on its surface areas from 701.5 (entry 1) to 362 m²/g (entry 2) upon modification with TETA and further to 85.6m²/g, (entry 3) when modified with PEHA. These results show that the presence of more amine functional groups in the surface decreases the surface area. The same trend can be observed for PSC, from 327.45m²/g reduces to 2.63m²/g, upon TETA surface modification. The total pore volume also decreases accordingly. These results indicate effective pore blockage in the micropores due to the presence of long chain of amine groups. Such decrease in surface area, attributed

to the incorporation of chains of nitrogen species to the micropores, create steric hindrances and partially block the entry of nitrogen gas (N₂) to small pores. These results suggest that the amine groups fill in the pore cavity resulting to smaller pore volume.

The CO₂ adsorption isotherms of the samples at 25°C and their corresponding calculated narrow micropore volume (Figure 9) indicate a slight increase in CO₂ adsorption between PSC and PSC-1 confirming the important role of amine functional groups. This suggests that the mechanism of adsorption is based on interaction of the CO₂, which is a weak Lewis acid with amines, suggesting chemisorption process.

Comparison of the PSC with the PSAC showed an increase in CO₂ adsorption. The shape of the isotherm of PSAC is more pronounced in terms of CO₂ capture due to a progressive widening of the micropore size during activation resulting to a higher surface area. This result suggests that the activation of carbon material promotes physisorption process.

Comparison of CO₂ isotherms of PSAC with amine modified PSAC samples (PSAC-1 and PSAC-2) revealed a more pronounced increase in CO₂ adsorption. At 1 atm and 293 K, the amount of adsorbed CO₂ on PSAC-1 (1.88 mmol/g) and PSAC-2 (2.38 mmol/g) show an increase of 116% and 173% adsorption compared to the original PSAC (0.87 mmol/g) sample. The results show that both chemisorption (increased amine groups) and physisorption (increased surface area) processes may be operating in these systems. It can be noticed that the relationship between the sample surface area and its CO₂ adsorption capacity is contrary to the physisorption concept that the higher the surface area, the higher adsorption would be observed. Data in this study showed that PSAC-2, with the lowest surface area of 85.6m²/g, has the highest CO₂ adsorption capacity confirming that chemisorption process in CO₂ capture predominates in amine modified samples. These results are indicated by the narrow micropore volume (W_0) calculation using Dubinin-Radushkevich (DR) method ($W = W_0 \exp[-k(e/\beta)^2]$). The calculated W_0 increases with increasing amount of nitrogen in amine: from 0.091 to 0.186 for PSAC-1, 0.212 for PSAC-2. Moreover, N₂ isotherm data of PSAC-2 indicates narrower pores size distribution and lower pore volume compared to PSAC. Thus, even if the micropore size and volume is narrow, there is a correlation between the microporosity of the adsorbent with CO₂ capture capacity. Furthermore, the CO₂ – adsorbent affinity depends not only on the high amount of total nitrogen incorporated into the carbon but also on the type of N-functionalities introduced, allowing chemisorption to operate predominantly thus capturing more CO₂ (Martin et al. 2010).

Since CO₂ is an acidic gas and possesses a strong quadruple moment, the increase of amine groups on the carbon surfaces will strengthen the interaction of CO₂ on the activated carbons (especially with nitrogen having moderately quadruple moment) and thus the adsorption capacity of activated carbons for CO₂ is improved. The proposed capture of CO₂ on aminated PSAC may occur via acid base interaction. Serna-Guerrero et al. (2008) described CO₂ capture mechanisms that give carbamate and bicarbonate products depending on the moisture content. Under dry conditions, carbamate is favourable; while, at higher relative humidity (RH), gradual formation of bicarbonate is possible. Generally, the reactivity of amines to CO₂ follows the order primary, secondary, and tertiary amines. The reaction of CO₂ with primary and secondary amine gives the zwitterion first before the carbamate is formed. The reaction of a tertiary amine with CO₂ forms bicarbonate and becomes favorable at high RH since water serves as a proton transfer agent in the reaction of CO₂ and amine groups (Bishnoi & Rochelle 2000; Xiao et al. 2000; Liao & Li, 2002).

The aminated PSAC sample presents a significantly enhanced CO₂ capture capacity due to the enhanced effect of a favorable surface chemistry.

CONCLUSION

This work presents, for the first time, the possibility of using agricultural waste Pili nut shell as a precursor of activated carbon and its use as an alternative source for CO₂ capture. An effective CO₂ adsorbent has been prepared by (1) chemical activation with NaOH, which increases the surface area and pore volume of the activated Pili nut shell, and (2) surface modification with amine, which increases the amount of amine groups on the carbon surface. The carbon material modified with higher nitrogen content had the highest adsorption capacity of CO₂. The amount adsorbed of CO₂ on the Pili nut shell samples from CO₂ sorption analysis followed this order: PSAC-2 > PSAC-1 > PSAC > PSC-1 > PSC. The CO₂ capture capacities at 25°C of the amine treated carbons increased with respect to the parent carbons. The amine treated samples having lower surface areas (362-2.63m²/g) gave the higher adsorption capacities of CO₂ against the parent carbon materials. This is due to the introduction of nitrogen groups on the surface that reacts covalently with CO₂. The adsorption of CO₂ on PSAC is a physical adsorption process while in the amine treated samples (PSAC-1 and PSAC-2) chemical adsorption process dominates.

To further realize the potential of the modified Pili nut shell activated carbon, a study on the performance

adsorption capacity of CO₂ via thermo-gravimetric analysis by varying the temperature and time as well as a study on the cycle regeneration process is underway. Moreover, a thorough assessment study needs to be done especially one that weighs the benefits gained from CO₂ capture against the wastes generated in producing the modified activated carbon.

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REFERENCES

- AHMAD AL, SUNARTI AR, LEE KT, FERNANDO WJN. 2010. CO₂ removal using membrane gas absorption. *Int J Greenh Gas Con* 4(3): 495-498.
- ARENILLAS A, RUBIERA F, PARRA JB, ANIA CO, PIS JJ. 2005. Surface modification of low cost carbons for their application in the environmental protection. *Appl Surf Sci* 252:619-624.
- BISHNOI S, ROCHELLE GT. 2000. Absorption of carbon dioxide into aqueous piperazine: Reaction kinetics, mass transfer and solubility. *Chem Eng Sci* 55: 5531-5543.
- BODEN TA, MARLAND G, ANDRES RJ. 2012. Global, Regional, and National Fossil-Fuel CO₂ Emissions. Oakridge, Tennessee, USA: Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy. Retrieved from http://cdiac.ornl.gov/trends/emis/overview_2009.html on 9 September 2013.
- BOEHM HP. 1994. Some aspects of the surface-chemistry of carbon blacks and other carbons. *Carbon* 32(5):759-69.
- BRANDANI FM, RUTHVEN DM. 2004. The effect of water in on the adsorption of CO₂ and C₃H₈ on type x zeolites. *Ind Eng Chem Res* 43: 8339.
- CHAFFEE AL, KNOWLES GP, LIANG Z, ZHANG J, XIAO P, WEBLEY PA. 2007. CO₂ capture by adsorption: Materials and process development. *Int J Greenh Gas Con* 1(1): 11-18.
- CORONEL RE. 1991. *Canarium ovatum* Engl. In: Plant Resources of South East Asia - No.2. Edible fruits and nuts. Verheij EWM, Coronel R.E, eds. Bogor, Indonesia: PROSEA Foundation. p105-108.
- FIGUEROA JD, FOUT T, PLASYNSKI S, MCILVRIED H, SRIVASTAVA RD. 2008. Advances in CO₂ capture technology—the U.S. Department of Energy's carbon sequestration program. *Int J Greenh Gas Con* 2(1): 9-20.
- GRAY ML, CHAMPAGNE KJ, FAUTH D, BALTRUS JP, PENNLIN H. 2008. Performance of immobilized tertiary amine solid sorbents for the capture of carbon dioxide. *Int J Greenh Gas Con* 2(1):3-8.
- HESCHEL W, KLOSE E. 1995 On the suitability of agricultural by-products for the manufacture of granular activated carbon. *Fuel* 74:1786-1791.
- LIAO CH, LI MH. 2002. Kinetics of absorption of carbon dioxide into aqueous solutions of monoethanolamine + N-Methyldiethanolamine. *Chem Eng Sci* 57: 4569-4582.
- LUAAC, YANG T. 2004. Effect of activation temperature on the textural and chemical properties of potassium hydroxide activated carbon prepared from pistachio-nut shell. *J Colloid Interface Sci* 274(2):594-601.
- MARTIN CF, PLAZA MG, PIS JJ, RUBIERA F, PEVIDA C, CENTENO TA. 2010. On the limits of CO₂ capture capacity of carbons. *Sep Purif Technol* 74:225-229.
- PLAZA MG, PEVIDA C, ARENILLAS A, RUBIERA F, PIS JJ. 2007. CO₂ capture by adsorption with nitrogen enriched carbons. *Fuel* 86:2204-12.
- PLAZA MG, PEVIDA C, PIS JJ, RUBIERA F. 2011. Evaluation of the cyclic capacity of low-cost carbon adsorbents for post-combustion CO₂ capture. *Energy Procedia* 4:1228-1234.
- PONDEVIDA JL. 2011. Production of Activated Carbon from Pili Shell. Taguig City:ITDI-DOST. 86p.
- PRZEPIÓRSKI J, SKRODZEWICZ M, MORAWSKI AW. 2004. High temperature ammonia treatment of activated carbon for enhancement of CO₂ adsorption. *Appl Surf Sci* 225:235-42.
- QUISUMBING E. 1978. Medicinal plants of the Philippines. Manila:Katha Publishing. p476-477.
- RAO AB, RUBIN ES. 2002. A technical, economic, and environmental assessment of amine-based CO₂ capture technology for power plant greenhouse gas control. *Environ Sci Technol* 36(20):4467-4475.
- SANGER SH, MOHOD AG, KHANDETODE YP, SHRIRAME HY, DESHMUKH AS. 2011. Study of carbonization for cashew nut shell. *Res J Chem Sci* 1(2):43-55.

- SERNA-GUERREO R, DA'NA E, SAYARI A. 2008. New insights into the interactions of CO with amine-functionalized silica. *Ind Eng Chem Res* 47(23): 9406-9412.
- SHAFEEYAN MH, DAUD WMAW, HOUSHMANDA, SHAMIRI A. 2010. A review on surface modification of activated carbon for carbon dioxide adsorption. *J Anal Appl Pyrolysis* 89(2):143-151.
- SIRIWARDANE R, SHEN M, FISHER E, POSTON J, 2001. Adsorption of CO₂ on molecular sieves and activated carbon. *Energy Fuels* 15(2): 279-284.
- TSENG RL. 2007. Physical and chemical properties and adsorption type of activated carbon prepared from plum kernels by NaOH activation. *J Hazard Mater* 147:1020-1027.
- TUINIER MJ, VANT SINT ANNALAND M, KUIPERS JAM. 2011. A novel process for cryogenic CO₂ capture using dynamically operated packed beds - an experimental and numerical study. *Int J Greenh Gas Con* 5(4): 694-701.
- WANG Q, LUO J, ZHON Z, BORGNA A. 2011. CO₂ capture by solid adsorbents and their applications: current status and new trends. *Energy Environ Sci* 4:42-55.
- XIAO J, LI CW, LI MH. 2000. Kinetics of absorption of carbon dioxide into aqueous solutions of 2-amino-2-methyl-1-propanol + Monoethanolamine. *Chem Eng Sci* 55:161-175.
- YAMASHITA Y, OUCHI K. 1982. Influence of alkali on the carbonization process—I: Carbonization of 3,5-dimethylphenol-formaldehyde resin with NaOH. *Carbon* 20(1):41-45.
- YOON SH, LIM S, SONG Y, OTA Y, QIAO W, TANAKA A, MOCHIDA I. 2004. KOH activation of carbon nanofibers. *Carbon* 42(8-9):1723-1729.
- ZHANG Z, XU M, WANG H, LI Z. J 2010. Enhancement of CO₂ adsorption on high surface area activated carbon modified by N₂, H₂ and ammonia. *Chem Eng* 160:571-577.
- ZONDLO JW. 2004. Turbostatic Carbon Powder. Morgantown, West Virginia, USA: West Virginia University. p 391-421. Retrieved from http://www.fischer-tropsch.org/DOE/DOE_reports/40350/40350-2004/40350-2004,%20Part%204,%20Pages%20391%20-%20647.pdf on 15 May 2012.