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Comparative Study of Natural Gas Adsorption Isotherms on KOH and H_3PO_4 Palm Kernel Shells Porous Activated Carbon

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Sustainable energy of Natural Gas (NG) has been an increasingly valuable and advantageous fossil fuel as it produces a cleaner combustion, and efficient consumption. Compressed Natural Gas (CNG) storage method and its utilisation has caused several problems due to high cost of installation for extensive 25.86 MPa high-pressure bulky cylinder, internal cylinder corrosion, and the possibility of releasing an explosive compressed gas. Adsorb Natural Gas (ANG) storage as a new technology, where natural gas is adsorbed in a suitable adsorbent with high porosity to increase the volume of gas stored in the vessel at lower pressure 3.45 – 5.52 MPa is a promising alternative. The energy density stored in ANG storage system is greater than the CNG vessel at the same pressure. Solid sustainable material of Palm Kernel Shell (PKS) was treated chemically to obtain adsorbent media to determine its adsorption and desorption rate performance at certain pressure. The adsorbent obtained by treatment with KOH and H_3PO_4 labelled as PKS-ACB and PKS-ACA. Samples were characterised by SEM, BET, TGA and FTIR. The SEM, BET, TGA and FTIR results showed promising results. The adsorption rate of the first 20 minutes was 0.038 mmol/g.min for PKS-ACA and 0.034 mmol/g.min for PKS-ACB. The desorption rate of PKS-ACA and PKS-ACB was 643 mmol/g.min and 430 mmol/g.min. There was no gas residual left in the sorbent. Findings highlighted that sustainable solid waste materials of palm kernel shell are renewable; its surface property as natural gas adsorbent storage known as ANG.

1. Introduction

Natural gas mainly composed of 85 - 95 mol% methane stored as CNG, between 20 - 25 MPa at room temperature (Esteves et al., 2008). CNG has disadvantages of requiring an expensive cost to maintain the high pressure vessels and multi-stage compressors (Wang et al., 2011) and only 29 % energy density of gasoline achieved at 20 MPa (Liu et al., 2014). Second method to store natural gas is liquefied natural gas (LNG), which requires -162 °C boiling points at atmospheric pressure of 101.35 kPa in cryogenic fluid form. Trained personnel are required to handle the cryogenic temperature of the system. LNG cryogenic process is not cost effective (Wang et al., 2011) and attained 72 % volumetric energy density of gasoline (Menon and Komarneni, 1998). Due to high costs, safety and operational restrictions of CNG and LNG, researchers are working towards reliable alternatives (Esteves et al., 2008). ANG is viewed as alternative technology to CNG and LNG. In ANG, the gas is adsorbed on the surface of porous activated carbon (AC) packed inside a vessel at lower pressure (Wang et al., 2011) of 3.5 – 4 MPa and at ambient temperatures. There would be an improvement in safety and cost of compression by using ANG system. Researches on adsorption on agricultural waste for industrial applications are dedicated towards developing cheaper adsorbents for ANG systems. Because of their possession of

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favourable surface area and pore volume, with diversified microporous structures (Delevar et al., 2012). The adsorptive characteristics of an activated carbon depends on the type and properties of the materials to be used as precursor resources, the activation method and nature of activating agent (Sren´scek-Nazzal et al.,2013). The aim of the present study is to synthesis and compare activated carbon from PKS using KOH and H_3PO_4 as an activating agent (Aroua et el.,2008) that can be used in ANG system for natural gas storage.

2. Experimental

2.1 Raw material pre-treatment

Raw PKS precursor was washed using deionised water to removed dirt particles. Dehydration step was done in an oven at 105 °C for 24 h prior to grind through 0.9 mm cutter gap of Retsch grinder machine model BB50. The particle material size obtained between 0.5 - 0.85 mm and then re-washed using deionised water and followed second dehydration of the same condition.

2.2 Bio-char material preparation

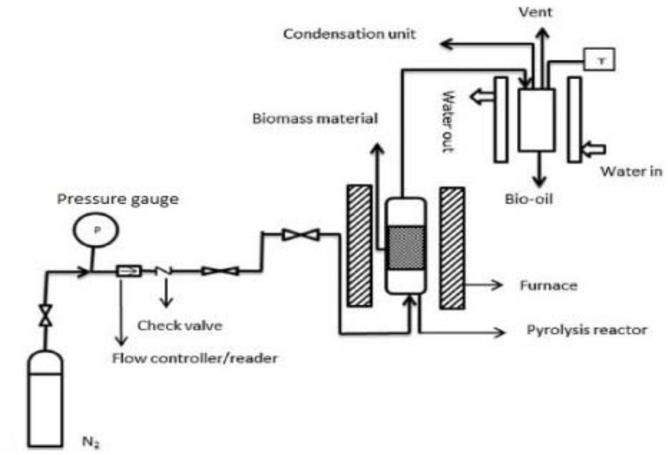


Figure 1: Schematic diagram of PKS precursor carbonisation test rig

Figure 1 shows the pyrolysis and carbonisation of 500 g of sieved PKS. The PKS was loaded into the stainless steel tabular reactor (5 cm i.d., 15 cm length). The process was done under nitrogen flow of 1 L/min in three steps includes; 10 °C /min heating rate preheating process, 730 ± 20 °C for 2 h carbonisation, and normal cooling step to ambient condition. The bio-char obtained was designated as PKS-BC which had the 0.5 - 0.85 mm particle size

2.3 Activated carbon acidic and alkali surface materials

50 g PKS-BC was impregnated with 2.0 M H_3PO_4 solution by the weight ratio of 1 : 5. The mixing was performed on the thermal stirrer at temperature 85 °C for period 2 h and stirring 6 RPM using 500 mL beaker. The slurry was filtered and dried in oven for 24 h at 105 °C, known as PKS char acidic (PKS-AC). The substrate product was further treated with 400 W microwave power level treatment to achieve activated carbon using 200 mL/min flow of nitrogen (Yang et al., 2010) then CO_2 for 10 min each gas as shown in Figure 2. The activated carbon sample was labelled as PKS-ACA. Microwave treatment process advantages were reported (Shen et al., 2008) that can shorten treatment period as compared to conventional heating procedure. Activated carbon acidic obtained was stored in opaque sampling bottle with O_2 and H_2O adsorbent gel to prevent oxidation of any metal and rehydrated mechanism. The process steps were repeated in order to prepare the alkali (base) surface sample, but 2 M KOH was used instead of 2.0 M H_3PO_4 with 1 : 2 weight ratio and the obtained alkali activated carbon was labelled PKS-ACB.

2.4 Physical Samples Characterisations

Brunauer, Emmett and Teller (BET) and Scanning Electron Micrograph (SEM) were used to characterise samples to identify the surface area, pore size, pore volume and the morphology images. BET used was the volumetric techniques (Micrometrics ASAP 2020). The surface area was determined by using the BET method but only adsorption data at relative pressure (P/P_0) range of 0.04 to 0.2 was considered (Usman et al., 2014). Karl Zeiss (EVO50 XVPSEM, Germany) of SEM has been used to study the surface morphology variation of sample’s particles structures after different treatments (Lozano-Castelló et al., 2002). The samples were dried at 100 °C and cooled down to ambient then were stored in desiccator for 12 h.

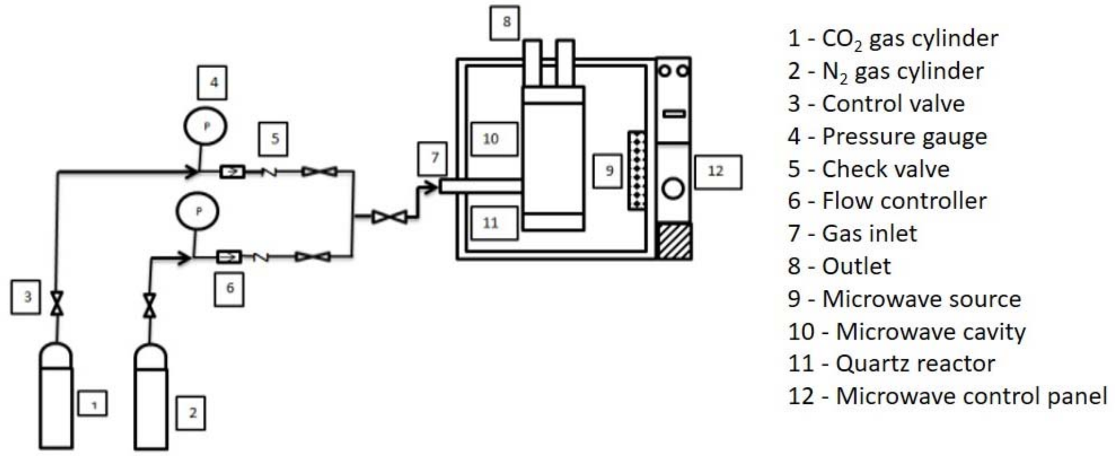


Figure 2: Schematic diagram of the microwave system

2.5 Chemical Samples Characterisations

Thermogravimetric analysis (TG/DGA) and Fourier Transform Infrared (FTIR) were used to determine the thermal decomposition effect and the presentation of surface functional group of samples using Fourier Transform Infrared (FTIR) spectroscope (FTIR-2000, PerkinElmer). TGA/DTGA was Mettler Toledo TGA/DSC1 and its mass loss was determined under nitrogen gas heating rate of 10 °C /min from temperature of 30 °C to 1,000 °C (Noor et al., 2014). The spectra from 4,000 to 400 cm^{-1} were recorded using Potassium bromine (KBr) pellets with 0.1 % carbon content. The activated carbon spectra provided an effective method that uses the standard IR spectra to monitor and identify the available functional groups on the samples surface.

2.6 Volumetric static methane (CH_4) adsorption and desorption

The static CH_4 adsorption and desorption procedures were adopted from works of (Li et al., 2010) in fixed bed unit (Figure 3). Samples including commercial activated carbon were tested for methane adsorption at gauge pressure of 689.48 kPa and constant 30 °C (Nasri et al., 2014). Prior to carry out the tests, activated carbon samples were dried in oven at 105 °C for 24 h. The unit was equipped with digital pressure transducer (Autonics PSA/PSB series), K-type thermocouple for continuous temperature monitoring, and vacuum pump for regeneration purpose. Tubing and fittings line were supplied by Swagelok stainless-steel quality and to ensure no leaking. The quantity of CH_4 adsorbed was obtained using the measured temperatures and pressures of the load and adsorption cells (Nasri et al., 2014).

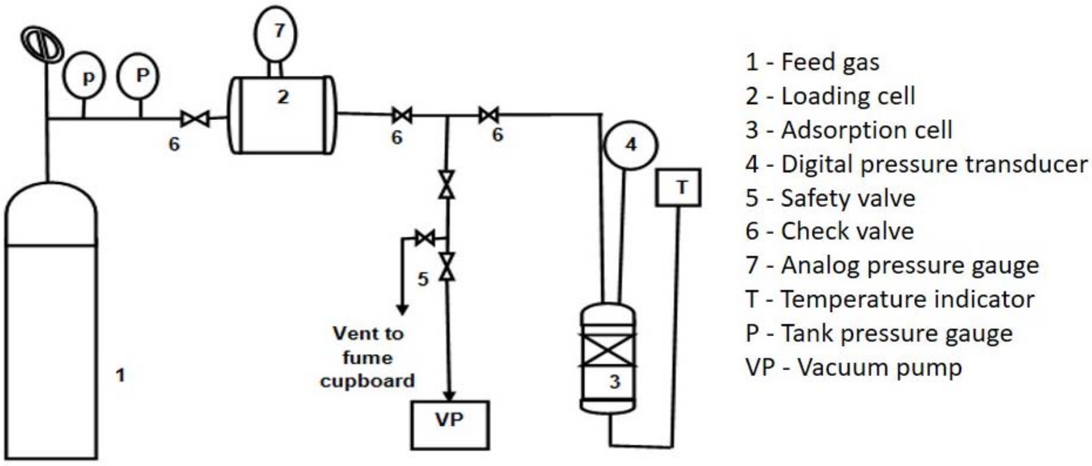


Figure 3: Schematic diagram of the volumetric static adsorption set-up

The methane (natural gas) was introduced to the loading cell until the pressure reaches the desired level. The gas was allowed to contact with the adsorbent by opening the valve between loading cell and adsorption cell. This measurement continues until the pressure of adsorption cell remains constant and was tested in three cycles. Eq1 below was applied to estimate the adsorption capacity in terms of measurable temperature and pressure values before and after equilibrium state (Ozdemier et al., 2002):

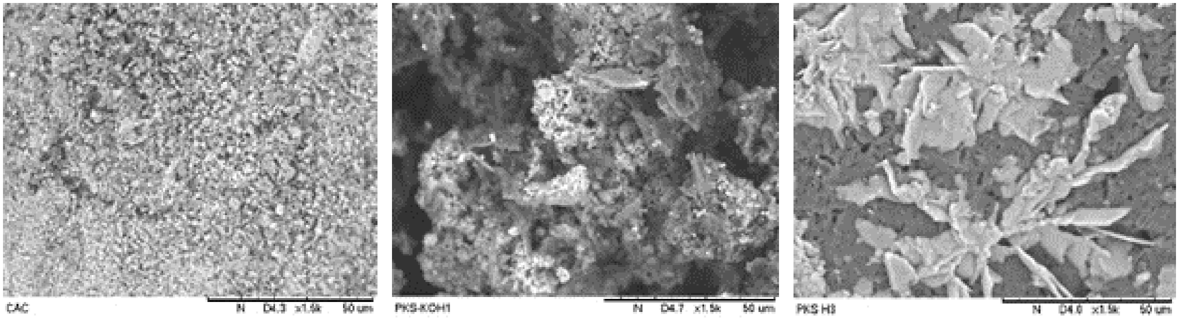
$$q = \frac{1}{m}\left[\frac{V_v}{R}\left(\left|\frac{P}{ZT}\right|_i - \left|\frac{P}{ZT}\right|_{eq}\right)_a + \frac{V_l}{R}\left(\left|\frac{P}{ZT}\right|_i - \left|\frac{P}{ZT}\right|_{eq}\right)_l\right] \tag{1}$$

where, P =pressure, T = temperature, V = volume, R = gas constant, a = adsorption cell, l = loading cell, I = initial state, eq = adsorption final equilibrium state, m = adsorbent mass, q = amount of gas absorbed, Z = compressibility factor.

3. Results and discussion

3.1 SEM and BET

SEM resulted that the activated carbon samples showed cavities over their surface (Figure 4(a)) which could be the reason on the ability of these activated carbon samples to absorb natural gas (methane). Pore surface was observed (Figure 4(b) and 4(c)) and this was happened due to the carbonisation that removed volatiles and produced a fixed carbon mass with only rudimentary (Hu et al., 2001). By visual comparison, the pores network and cavities distribution happened over the surface of all samples.



(a) (b) (c)

Figure 4: SEM zoomed 1.5 K for (a) Commercial-AC, (b) PKS-ACB, and (c) PKS-ACA

BET results as shown in the Table 1 for PKS-ACB treated by KOH and PKS-ACA of acidic surface which has the high and low surface area and pores volume of both samples. Surface area and textural properties of porous material plays crucial role in activated carbon sorption capacity. After activation of the sample, there was a positive improvement in both surface area and pore volume (Hesas et al., 2015).

Table1: Porosity parameters of activated carbon obtained from nitrogen adsorption.

Samples	BET (m^2/g)	V_{Total} (cm^3/g)	V_{micro} (cm^3/g)
PKS-ACB	270.7027	0.11050	0.09779
PKS-ACA	4.7189	0.00548	0.00001

3.2 TG/DGA and FTIR

Hemicellulose, cellulose and lignin removal in palm shells materials could attribute to the pyrolysis thermal decomposition (Li et al., 2008). The thermal decomposition TG/TGA effect has involved three main stages; moisture removal, de-volatilisation and continuous slight de-volatilisation (Idris et al., 2010). The TG/DGA evolution profiles of PKS was explained in detail by Usman (2016). FTIR resulted the spectra of the samples displayed (Figure 5) the bands 3,200 – 3,600 cm^{-1}correspond to O-H stretch in alcohols; 1,800 - 1,400 cm^{-1} is assigned to C=C stretch aromatics; the weak bends at 1,300 - 1,000 cm^{-1} could be due to C-O groups as reported by Usman, (2016). There are some spectra present in the commercial activated carbon but absent in the porous carbons produced. This could be related to the components naturally exist on the surface of the material and added components during chemical treatment.

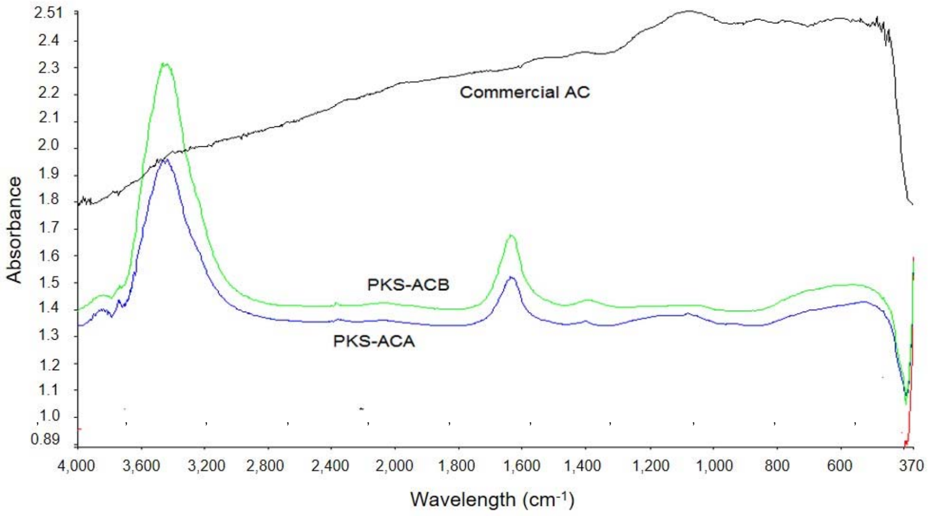


Figure 5: The FTIR spectra of the raw palm kernel activated carbon produced

3.3 Natural Gas adsorption and desorption

Natural gas adsorption on PKS-ACB, PKS-ACA was studied at gauge pressure of 689.48 kPa as shown in Figure 6. In this work, the adsorption of natural gas was studied on all the activated carbon. The adsorption was fast and high within the first 20 minutes on both of the activated carbon as shown in Figure 6. The adsorption rate, slowly decrease after the first 20 minutes. Low surface area, and pore volume lowered the adsorption capacity of the adsorbent as shown in the results. The result also showed high adsorption uptake on KOH activated carbon than H_3PO_4 activated carbon. High pressure is directly proportional to the high uptake of natural gas as stated by Delavar et al. (2012), high pressure act as a driver for adsorption process.

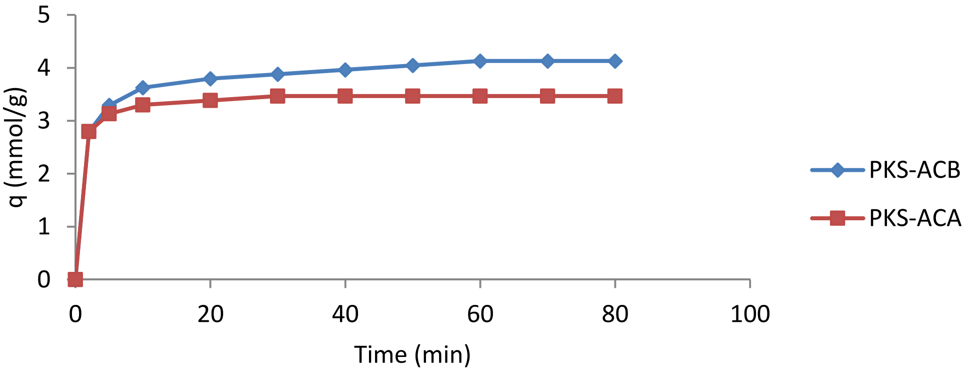


Figure 6: Natural gas adsorption with respect to time

4. Conclusions

Findings highlight the potentials of palm kernel shells to be the base material for adsorbent preparation and its advantages in natural gas storage (ANG) compared to CNG. PKS activated carbon showed the development of porosity in the materials after carbonisation and microwave activation as shown in SEM and BET results. BET results showed that the total pore volume of PKS activated carbon is high and within the micro-pore range, which implies that it is suitable for gas phase adsorption applications.

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References

Aroua M.K., Wan Daud W. A., Yin C.Y., Adinata D., 2008, Adsorption capacities of carbon dioxide, oxygen, nitrogen and methane on carbon molecular basket derived from polyethyleneimine impregnation on microporous palm shell activated carbon, Separation and Purification Technology 62, 609-613.

Delavar M., Ghoreyshi A.A., Jananshahi M., Khalili S., Nabian N., 2012, The effect of chemical treatment on adsorption of natural gas by multi-walled carbon nanotubes: sorption equilibria and thermodynamic studies, Chemical Industry & Chemical Engineering Quarterly 18, 193-207.

Esteves I.A.A.C., Lopes M.S.S., Nunes P.M.C., Mota J.P.B., 2008, Adsorption of natural gas and biogas components on activated carbon, Separation and Purification Technology 62, 281-296.

Hesas R.H., Arami-Niya A., Wan Daud W.M.A., Sahu J.N., 2015, Microwave-assisted production of activated carbons from oil palm shell in the presence of CO_2 or N_2 for CO_2 adsorption, Journal of Industrial and Engineering Chemistry 24, 196-205.

Hu Z., Srinivasan M.P., Ni Y., 2001, Novel activation process for preparing highly microporous and mesoporous activated carbon, Carbon 39, 877-886.

Idris S.S., Abd Rahman N., Ismail K., Alias A., Abd Rashid Z., Aris M.J., 2010, Investigation on thermochemical behaviour of low rank Malaysian coal, oil palm biomass and their blends during pyrolysis via thermogravimetric analysis (TGA), Bioresource Technology 101, 4584-4592.

Li F., Yi H., Tang X., Ning P., Yu Q., 2010, Adsorption of Carbon dioxide on Coconut Shell Activated Carbon, International Conference on MASS, 24-26th August 2010, Wuhan, China.

Li W., Yang K., Peng J., Zhang L., Guo S., Xia H., 2008, Effects of carbonization temperatures on characteristics of porosity in coconut shell chars and activated carbons derived from carbonized coconut shell chars, Industrial Crops and Products 28, 190-198.

Liu B., Wang W., Wang N., Au C.T., 2014, Preparation of activated carbon with high surface area for high-capacity methane storage, Journal of Energy Chemistry 23, 662-668.

Lozano-Castelló D., Alcañiz-Monge J., de la Casa-Lillo M., Cazorla-Amorós D., Linares-Solano A., 2002, Advances in the study of methane storage in porous carbonaceous materials, Fuel 81, 1778-1779.

Menon, Komarneni, 1998, Porous adsorbents for vehicular natural gas storage: a review, Journal of Porous Materials 5, 43-58.

Nasri N.S., Usman D.H., Amin N.A.S., Ahmed M.M., Jibril M., 2014, Methane adsorption on chemically modified microwave irradiated palm shell porous carbon, Advanced Materials Research 1043, 175-179.

Ozdemier E., Schroeder K., Morsi B.I., 2002, Effect of swelling on the adsorption isotherm of carbon dioxide on coal, Fuel Chemistry Division Preprints 47, 12-13.

Shen W., Li Z., Lieu Y., 2008, Surface chemical functional groups modification of porous carbon, Recent Patents on Chemical Engineering 1, 27-40.

Sren´scek-Nazzal J.S., Kamin´ska W., Michalkiewicz B., Koren Z.C., 2013, Production, characterization and methane storage potential of KOH-activated carbon from sugarcane molasses, Industrial Crops and Products 47, 153-159.

Usman D., Siti N., Murtala M., Rahmat Mohsin, Noor N.S., 2014, Assessment of porous carbons derived from sustainable palm solid waste for carbon dioxide capture, Journal of Cleaner Production 71, 148-157.

Usman D.H, 2016, Palm-Polyetheretherketone Porous Carbons as Sorbents For Gas Adsorption Applications, PhD Thesis, Universiti Teknologi Malaysia, Johor Bahru, Malaysia.

Wang Y., Hashim M., Ercan C., Khawajah A., Othman R., 2011, High Pressure Methane Adsorption on Granular Activated Carbons. 21st Annual Saudi-Japan Symposium Catalysts in Petroleum Refining & Petrochemicals Dhahran, 27-28th November 2011, Saudi Arabia.

Yang K., Peng J., Srinivasakannan C., Zhang L., Xia H., Duan X., 2010, Preparation of high surface area activated carbon from coconut shells using microwave heating, Bioresource Technology 101, 6163-6169.