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CO_2 Adsorption Isotherms on KOH, H_3PO_4 and $FeCl_3.6H_2O$ Impregnated Palm Shell Kernel Activated Carbon

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Commercial sorbents available are expensive as a result of using high cost and non-renewable materials as precursors. It is imperative to select cheap, viable and sustainable carbon source for production of adsorbents for subsequent use in adsorption applications. Palm kernel shell char was obtained by carbonisation process at 730 °C ± 20 °C for 2 h with 10 °C/min heating rate under inert gas flow. The bio-char obtained was further grinded and sieved to 0.5 to 0.85 mm, then treated and synthesised separately each sample by KOH, H_3PO_4 and $FeCl_3.6H_2O$ solution with ratio 1 : 1 weight ratio and followed by microwave treatment technique. Samples treated with chemicals used were named as PKS-POT (Palm Kernel Shell with Potassium Hydroxide), PKS-PAP (Palm Kernel Shell with Phosphoric acid) and PKS-FER(Palm Kernel Shell with Ferric chloride hexahydrate). CO_2 gas was used during the adsorption and desorption study. Samples were characterised by Brunauer–Emmett–Teller (BET), scanning electron microscope (SEM) and Fourier transform infrared spectroscopy (FTIR). PKS-POT showed highest BET surface area (208.7037 m^2/g) and pore volume (0.06580 cm^3/g). PKS-POT's SEM result also confirms large surface area, pores and more compact of the shell structure which related to high adsorption capacity compared to PKS-PAP and PKS-FER. CO_2 PKS-POT, PKS-PAP and PKS-FER adsorption capacities were 2.19, 0.62 and 1.25 mmol/g and no CO_2 gas left for the end desorption phase. From the study concluded that sustainable palm kernel shell material was successfully achieved to obtain the high surface area, high porosity and high adsorption sorbent capacity.

1. Introduction

Palm oil is one of the most important sustainability products which drive Malaysia to become world largest exporter and strengthen the agriculture and economy sectors. Malaysia is second largest producer of oil palm being responsible for 39 and 44 % of world production of palm oil and total exports around the globe (MPOB, 2010). Palm oil mills can produce many products such as palm kernels, fibre, and empty fruit bunches. All these products can be considered as sustainable product as It has the ability of becoming renewable energy source and also can be converted from dried oil palm wastes into the products which contain various values. Adsorption has proven to be one of most effective and economical technique applied today for the fact that it can happen at ambient temperature and low pressures. This tells a lot about its safety and economics. Air purification also activated carbon is being used in controlling potential harmful, environmental damaging and unpleasant odours (Arena et al., 2016). The use of this cheap, viable and readily available carbon source for

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production of activated carbon for subsequent use in the adsorption of acid gases will go a long way in promoting environmental pollution mitigation and waste management which helps in environmental sustainability and in turn curb the potential danger it poses to health. The development and advancement in green technology have further emphasise the need to harness renewable and sustainable waste materials in the country (Foo and Hameed, 2012). Wastes from agricultural sources are being utilised in the production of activated carbon as a strategy in pollution control. Environmental problems associated with agro-waste accumulation, air and water pollution are solved by conversion of these wastes to value added end products such as activated carbon (Nor et al., 2013). Activated carbons have become the most promising and effective adsorbent due their large surface area and relatively high sorption capacity, for a wide variety of applications (Mahmood et al., 2016). Activated carbon AC preparations from wastes is vital for the regional economy when products of high value are obtained from low cost materials. These bring about the solution to problem of wastes management (Gómez et al., 2016).

2. Experimental

2.1 Bio-Char and Activated Carbon Preparation

500 g of 0.5 - 0.85 mm sieved palm kernel shell (PKS) was loaded into stainless steel tabular reactor (5 cm i.d, 15 cm length) for the pyrolysis and carbonisation process in order to produce bio-char. This was done at 1 L/min nitrogen flow in three steps of 10 °C/min heating rate process, 730 °C ± 20 °C for 2 h carbonisation, and normal cooling step to ambient condition. Details of carbonisation process was taken from our previous work (Nor et al., 2013). 50 g PKS-bio-char each was impregnated with 2.0 M KOH, H_3PO_4 and $Fe_2Cl_3.6H_2O$ solution by weight ratio of 1 : 5. To have homogenous solutions, each sample was performed thermal stirring at 85 ˚C for period 2 h, 6 RPM using 500 mL beaker. The slurry was then filtered and oven dried at 105 ˚C for 24 h. Each substrate products were further dried 105 ^{o}C overnight and treated with 400 W microwave power level to achieve activated carbon using 200 mL/min each nitrogen (Yang et al., 2010) then CO_2 for 10 mins. The activated carbon samples were labelled PKS-POT, PKS-PAP, and PKS-FER.

2.2 Material Characterisation

2.2.1 BET and SEM Physical Samples Characterisations

BET, (Micrometrics ASAP 2020) and SEM were used to identify the surface area, pore size, pore volume and the morphology images. BET surface area was calculated by using the adsorption data at relative pressure (P/P_0) range of 0.04 to 0.2 (Hai, 2016). Karl Zeiss (EVO50 XVPSEM, Germany) of SEM has been used to study the surface morphology variation of sample's particles structures after different treatments (Nasri et al., 2014b).

2.2.2 TG/TGA and FTIR Chemical Samples Characterisations

The thermogravimetric analysis (TG/DGA) was determined and explained in detail by Nasri et al., (2014b). TG/DGA used was Mettler Toledo TGA/DSC1 and nitrogen gas at heating rate 10 ^{o}C/min from temperature of 30 ^{o}C to 1,000 ^{o}C (Nor et al., 2013) was applied for identifying its mass loss. FTIR was used to determine the present of surface functional components group of samples. The spectra from 4,000 to 400 cm^{-1} were recorded using Potassium bromine (KBr) pellets with 0.1 % carbon content.

2.3 Carbon dioxide volumetric static adsorption and desorption

CO_2 adsorption and desorption procedures were culled from works of Nasri et al. (2014a) in fixed bed of static volumetric unit. The CO_2 adsorption and desorption rate was measured at pressure 690 kPa and constant 30 ˚C as adopted testing procedure. The test rig comprises of digital pressure transducer (Autonics PSA/PSB series), thermocouple K-type, and vacuum pump for regenerate and desorb purpose. Swagelok tubing and fittings line were installed and fixed to ensure no leaking. measurements of Pressure and temperature in the loading cell and adsorption cell were used to obtain CO_2 adsorbed as adopted by methane procedures (Fatemi et al., 2011).

The mass balance adsorption equations in terms of measurable temperature and pressure quantities before and after equilibrium state can be determined using Ozdemir et al. (2002) equation as shown in Eq (1):

$$Q = 1/m\ (V_V/R\ (|P/ZT|_i - |P/ZT|_{eq})_a + V_l/R\ (|P/ZT|_i - |P/ZT|_{eq})_l) \qquad (1)$$

3. Results and discussion

3.1 SEM and BET

SEM results show that the activated carbon of all samples showed cavities over their surfaces (Figure 1(a)-(d)) in which the cavities pore volume have the potential and the ability to absorb gases including CO_2. The pores surface existed due to the carbonisation mechanism process that removed volatiles and moisture blocking the pores and produced a fixed carbon mass as the only rudiments (Hamza et al., 2016).

BET results as shown in the Table 1 for PKS-POT treated by KOH has the highest and surface area and pores volume. These can be attributed to alkaline chemicals being more effective in creating pores and interstices for the produced char than the other chemicals used. Surface area, surface chemistry and textural properties of porous material plays crucial role in activated carbon sorbent capacity. The surface area and pore volume of samples both improved after activation which could be as a result of formation of new pores, collapse of large pores to sizes suitable for accommodation of CO_2 molecules or development of interstices on particle surfaces to further enhance accommodation of CO_2 molecules (Hesas et al., 2015).

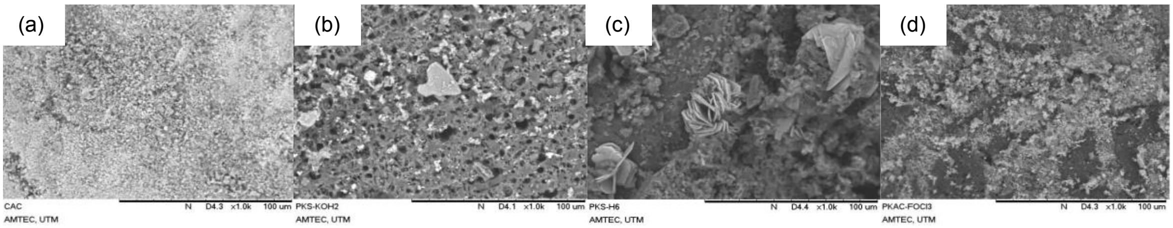


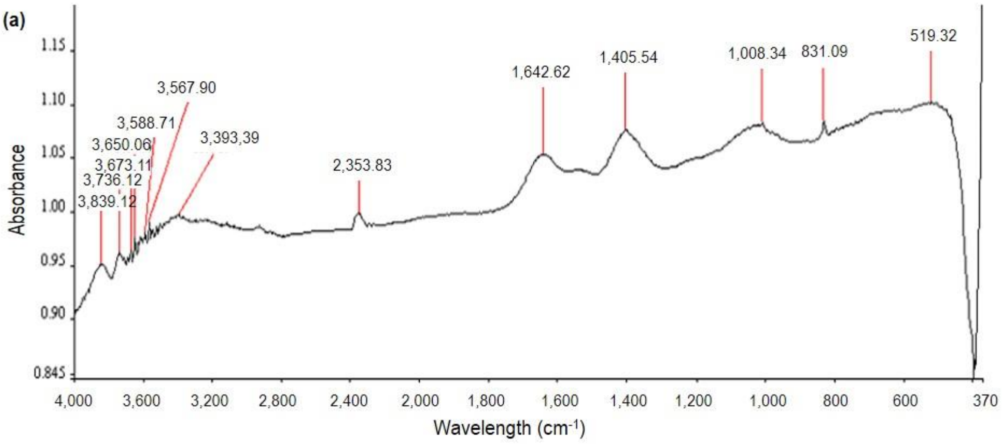
Figure 1: SEM micrographs x1,000 for (a) Commercial-AC, (b) PKS-POT, (c) PKS-PAP, and (d) PKS-FER

Table1: BET Porosity parameters of activated carbon

Samples	BET (m^2/g)	V_{Total} (cm^3/g)
PKS-POT	270.7027	0.06580
PKS-PAP	4.7189	0.00548
PKS-FER	68.7169	0.03330

3.2 TG/DGA and FTIR

Raw PKS precursor contains hemicellulose, cellulose and lignin which are lost during pyrolysis thermal decomposition. Moisture drying, main de-volatilisation and continuous slight de-volatilisation are the three main stages of the thermal decomposition in TG/DGA mechanism process (Zhang et al., 2017). Usman (2016) discussed in detail the TG/DGA evolution profiles of PKS. FTIR analysed by Usman (2016) mentioning that the spectra of the samples displayed (Figure 2 and Table 2) where the 3,200 – 3,600 cm^{-1} bands correspond to alcohols of O-H stretch; band 1,800 – 1,400 cm^{-1} C=C stretching for aromatics; the weak bands at 1,300 – 1,000 cm^{-1} could be related to C-O groups. The samples in study showed that the region of 3,393 - 3,629 cm^{-1} indicated the presence of O-H stretching due to presence of water molecules inside the activated carbon (Sadeek et al., 2014). The characteristic of C-H of CH_3 unit can be observed in the range of 2,351 – 2,356 cm^{-1}. The corresponding band that presence in the range of 1,640 – 1,642 $cm^{-1}$was attributed as the COO^- and acetate group. The C-O, C-C and C-N stretching vibration in all the activated carbon was observed in the range of 1,008 – 1,026 cm^{-1}. The peak at 831.09 cm^{-1} was only present in the PKS-POT due to the –CH bending between phenyl and COO. The medium –O stretching together with ring deformation are lying in the range of 519 - 539 cm^{-1}.



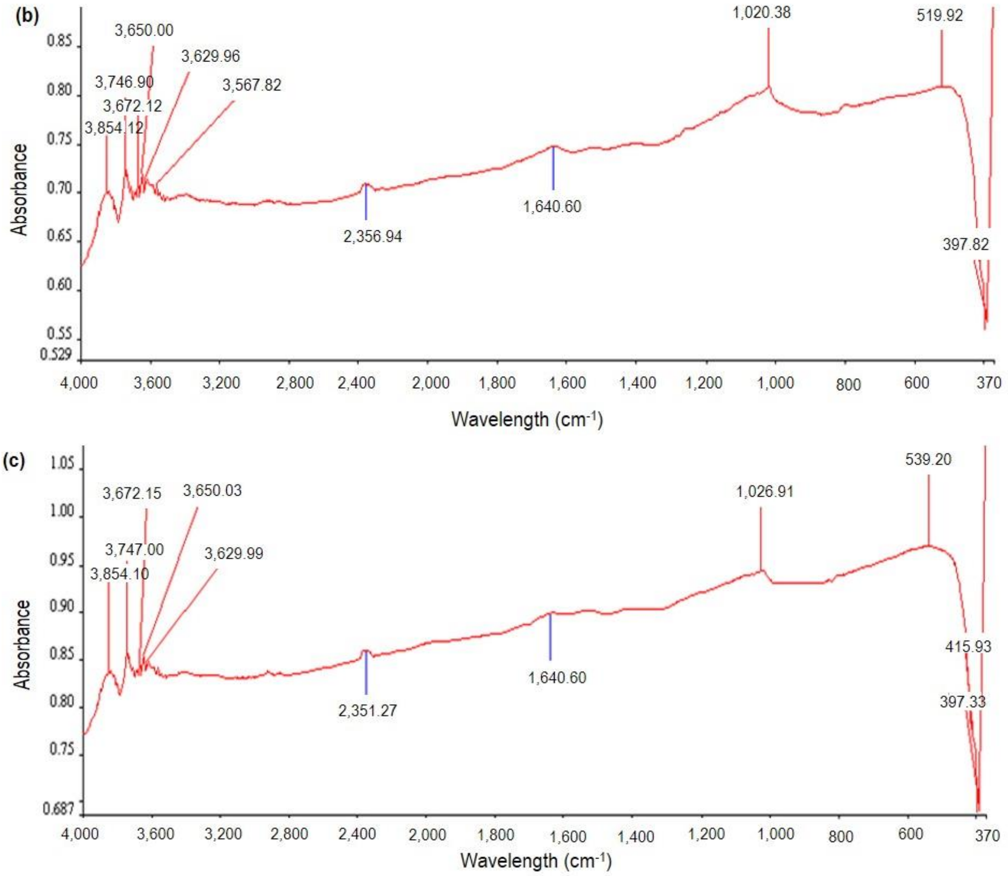


Figure 2: The FTIR spectra of the PKS activated carbon; (a) PKS-POT, (b) PKS-PAP, (c) PKS-FER

Table 2: FTIR frequencies (cm^{-1}) and tentative assignments of Figure 2

PKS-POT	PKS-PAP	PKS-FER	Assignments
3,393	3,567	3,629	OH stretching
2,353	2,356	2,351	C-H stretching
1,642	1,640	1,640	COO^- stretching
1,008	1,020	1,026	C-O, C-N and C-C stretching
519	519	539	Medium-O stretching and ring deformation
831	-	-	-CH bending

3.2 Natural Gas adsorption and desorption

CO_2 gas absorbed on PKS-POT, PKS-PAP, and PKS-FER were determined at 690 kPa and each sample was run for 3 different cycles as shown in Figure 3 where approximately the same with slight increase for each cycle. The value of carbon dioxide absorbed by PKS-FER, PKS-PAP, and PKS-POT were 0.62, 1.25, and 2.19 mmol/g (Table 3). PKS-POT has highest adsorption rate due to the highest BET surface area, total pore volume and the alkalinity of the sorbent surface. Carbon dioxide is more favourable to KOH because of the affinity existing between CO_2 (lewis acid) and KOH (base) as experimented by Shafeeyan et al. (2015) where NH_3 was used in place of KOH . CO_2 adsorption on H_3PO_4 surface activated carbon (sample PKS-PAP) was low because it could not form an interaction with CO_2 as both of them are acidic.

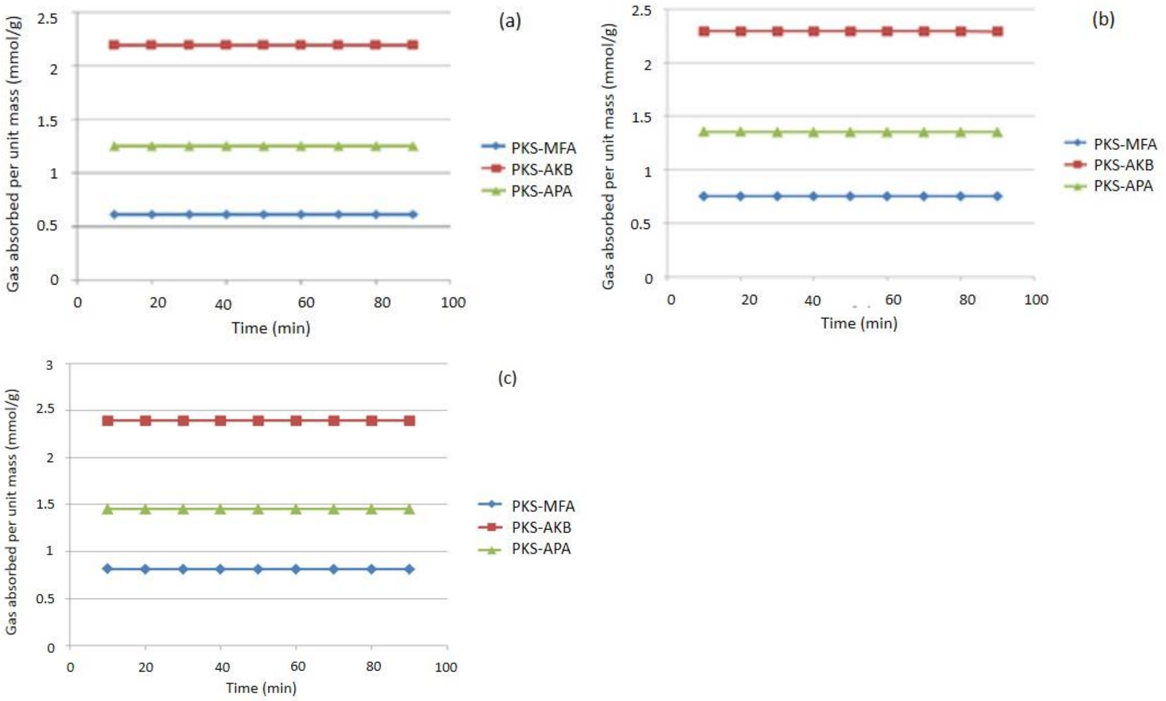


Figure 3: Respective natural gas adsorption with time; (a) 1st round, (b) 2nd round, (c) 3rd round of adsorptions

Table 3: Natural gas adsorption rate

Adsorption Rate (mmol/g adsorbent/min)		
PKS-POT	PKS-PAP	PKS-FER
2.19	1.25	0.62

Table 4: Natural gas desorption cycle with respect to time (min)

Sample	Time (min)		
Rounds	1st	2nd	3rd
PKS-POT	1.44	1.40	1.38
PKS-FER	1.32	1.20	1.30
PKS-PAP	1.11	1.14	1.09

Table 4 shows desorption of three cycle times for all samples. It can be observed that PKS-POT showed the slowest time during desorption mechanism process as compared to others. This is due to the binding surface energy between CO_2 and the surface alkali on PKS-POT which must be overcome for desorption to occur. On the contrary, sample PKS-PAP showed the fastest desorption cycles where it can be concluded to be the result of repulsion between surface acid H_3PO_4 of PKS and CO_2 acid gas.

4. Conclusion

Palm kernel shell precursor has good potential as raw sustainable material for an adsorbent ability to minimise the impact of CO_2 to atmosphere and global warming effect. KOH was found to be an effective chemical for activation in order to obtain PKS-activated carbon due to its ability to impart alkaline surface on activated carbon providing additional affinity for CO_2 capture. Chemical synthesising and microwave treatments on the porous bio-char PKS can enhance the chemistry surface and its property as good adsorbent material. The cavities activated carbon PKS implies that it is suitable for gas phase adsorption applications.

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