

Parametric Study of Concurrent Activation and Surface Modification (CAM) Process for Palm Kernel Shell Derived Activated Carbon

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This study aims to determine the process synthesis parameter for a concurrent activation and surface modification (CAM) process to produce activated carbon (AC) from palm kernel shell (PKS). It is targeted to obtain high impregnation of metal functionalized group on the AC for adsorption of acid gas. The process uses sulphuric acid (H₂SO₄) and barium chloride (BaCl₂) as activating agent and surface modification agent. The impregnated barium amount in AC was determined by inductively coupled plasma-optical emission spectrometry (ICP-OES) and X-ray fluorescence (XRF). This study utilized a batch process under different acid mass loading and activation temperatures. The ICP-OES analysis results showed that AC treated with 10 % H₂SO₄ at various activation temperatures (400-700 °C) exhibited high impregnated barium amounts ranging from 1.24 to 2.98 wt%. The XRF analysis also shows high impregnated barium amount ranging from 27.44-35.46 wt% for AC prepared at similar conditions. This manifests that lower acid mass loading ascribed to lower barium sulphate (BaSO₄) formation after surface modification with BaCl₂, which then facilitates porous structure development in PKS derived AC (PKSdAC) and sintering of barium metal on its surface during CAM by preventing sealing of pores by unreacted BaSO₄ and barium sulphide (BaS) after washing of AC.

1. Introduction

The concurrent activation and surface modification (CAM) process is a single-step simultaneous process of combining activation and surface modification of starting precursor into a carbon-enriched material (also termed activated carbon (AC)). Alternative to traditional chemical activation followed by the subsequent surface modification process, a single-step chemical activation with metal salt (i.e., iron chloride (FeCl₃) (Tian et al., 2019), barium chloride (BaCl₂) (Ajani et al., 2019), aluminium chloride hexahydrate (AlCl₃•6H₂O) (Sun et al., 2014), and manganese chloride tetrahydrate (MnCl₂•4H₂O) (Sun et al., 2014)) has been a growing interest recently to synthesize biomass-based AC because of it has a lower cost, is more environmentally friendly, can produce AC with adsorptive and magnetic properties. In contrast to the metal salt, the traditional activating agents are typically strong bases and acids by requiring stricter security measures for discharge and increasing synthesis process cost due to high consumable price and additional steps for further chemical modification process. Palm kernel shell (PKS) found potential as candidate for producing porous AC (Nasri et al., 2017) because of its high carbon (Yang et al., 2004), high lignin (Sohni et al., 2018), high volatile materials (Yang et al., 2004), low ash content (Yang et al., 2006), low cost, and highly abundant. PKS is commonly disposed of in open dumps around the oil palm plantation estate or openly burned after crude oil production which produces a negative impact on the environment. Chen et al. (2019) and Cazetta et al. (2016) synthesized eucalyptus wood-based AC and coconut shell derived AC using FeCl₃. The synthesized FeCl₃-derived AC from eucalyptus wood exhibited a surface area of 645.23 m² g⁻¹ while 372 m² g⁻¹ for AC from coconut shell. Amuda and Ibrahim (2006) reported that the coconut shell derived AC prepared using BaCl₂ as activating agent presented a surface area

of 632 m² g⁻¹. Sun et al. (2014) investigated that *Arundo donax* Linn derived AC produced *via* chemical activation possessed high surface area with 1,156 m²g⁻¹ when incorporated phosphoric acid (H₃PO₄) with metal salt FeCl₃•6H₂O, 992 m² g⁻¹ with AlCl₃•6H₂O, and 1,332 m² g⁻¹ with MnCl₂•4H₂O.

There are a small number of studies investigate the production of biomass-based AC using a single-step chemical activation with metal salts (Cazetta et al., 2016) and the use of barium salts (Hidayu and Muda, 2017) for surface modification of activated carbon. With the shortcomings, in this present work, the objective is to prepare an AC derived from PKS using sulphuric acid (H₂SO₄) as activating agent incorporated with BaCl₂ as the modifying agent through the CAM process. BaCl₂ is selected as the modifying agent which is preferable to use with H₂SO₄ to generate the formation of barium sulphate or barite (BaSO₄), main source of barium (Ba) for PKS derived AC through its reduction process under thermal activation (Balintova et al., 2017). Presence of Ba salt is essential for PKS derived AC to create chemical adsorption with CO₂. The discharge of BaSO₄ is also practically nontoxic to invertebrates, plants, or wildlife (Menzie et al., 2008). A parametric study on the synthesis of PKS derived AC (PKSdAC) is performed by varying the H₂SO₄ mass loading and activation temperature. The effects of H₂SO₄ mass loading and activation temperature on the amount of Ba impregnated in AC were evaluated to investigate the potential process parameters for the CAM process of PKS. Inductively coupled plasma-optical emission spectrometry (ICP-OES) and X-ray fluorescence (XRF) were carried out to characterize the amount of impregnated Ba in AC for comparison.

2. Materials and methods

2.1 Materials

The PKS was selected as starting precursor for the preparation of AC in this study. PKS was collected from Lambir palm oil mill that is located in Miri Sarawak, Malaysia. H₂SO₄ (95-98 % purity, R&M) was used as the activating agent for AC preparation. BaCl₂ (≥ 99 % purity, Merck) was selected as the modifying agent for surface modification of PKS using together with H₂SO₄ to develop the formation of BaSO₄ to initiate its reduction process in the presence of carbon during heating for producing barium (Ba) functional group on AC.

2.2 Preparation of activated carbon via CAM process

First, the PKS was grinded into 2 mm particle size using a rotor mill and cleaned under running tap water several times to remove sand and impurities. The PKS was then dried in the oven at 105 °C for 24 h to remove any surface moisture. After drying, PKS was mixed with H₂SO₄ solution with the ratio 1:0.10 (mass basis) and soaked for 48 h at room temperature. The acid-treated PKS was filtered from the H₂SO₄ solution using vacuum filtration and then dried at 110 °C over 8 h to remove the excess acid on its surface. The dried acid-treated PKS was soaked for another 24 h in BaCl₂ solution with mass ratio of 1:0.10 at room temperature for the surface modification process. The BaCl₂ impregnated acidified PKS was obtained by undergoing vacuum filtration and was then dried in the oven at mild temperature of 70 °C to remove excess BaCl₂ on its surface to prevent overheating of the impregnated PKS interior structure from further causing enlarged pores in the resultant activated carbon during thermal CAM process. The BaCl₂ impregnated acidified PKS was then transferred into an electrical muffle furnace to carry out the CAM process by heating to 700 °C in the presence of ambient air. The furnace was kept at this temperature for about 2 h with a heating rate of 10 °C/min. After the CAM process, the furnace was cooled. The resultant activated carbon was collected and washed repeatedly for several times with distilled water and tap water to remove residual chemicals until the pH of residual reached between 7 and 8. The wet activated carbon was dried at 110 °C for 24 h to remove any moisture. The palm kernel shell derived activated carbon (PKSdAC) synthesis process was repeated by adjusting the H₂SO₄ mass loading from 10 % to 30 % and activation temperature from 700 °C to 400 °C and 550 °C. The list of PKSdAC prepared in this study at different H₂SO₄ mass loading (x, %) and activation temperature (T, °C) is shown in Table 1.

Table 1: List of PKSdAC prepared via CAM

Sample name (CxH ₂ SO ₄ -PKSdAC-T)	H ₂ SO ₄ mass loading (%)	Activation temperature (°C)
C10H ₂ SO ₄ -PKSdAC-400	10	400
C10H ₂ SO ₄ -PKSdAC-550	10	550
C10H ₂ SO ₄ -PKSdAC-700	10	700
C30H ₂ SO ₄ -PKSdAC-400	30	400
C30H ₂ SO ₄ -PKSdAC-550	30	550
C30H ₂ SO ₄ -PKSdAC-700	30	700

2.3 Characterization of PKSdAC

The amount of Ba impregnated in the PKSdAC from its surface up to interior pores prepared from the CAM process was determined using inductively coupled plasma-optical emission spectrometry (ICP-OES). The samples undergo wet acid digestion in accordance with USEPA 3050 B method by heating in nitric acid (HNO_3) using a hot plate open vessel prior to the ICP-OES analysis. A quantitative analysis of Ba element present in the PKSdAC was also evaluated using X-ray fluorescence (XRF) spectroscopy. The PKSdAC was grinded and the XRF was used to determine Ba content on the powered AC surface without performing sample dilution prior to the analysis as contrast to ICP-OES.

3. Result and discussions

3.1 Impregnated Ba element in PKSdAC from CAM process

Figures 1 investigated the effects of activation temperature on the impregnated Ba amount in CAM-PKSdACs for different H_2SO_4 mass loading (10 % and 30 %) analyzed using ICP-OES and XRF. 10 % and 30 % H_2SO_4 mass loading and activation temperature from 400-700 °C were selected for the CAM process based on the earlier research work for H_2SO_4 activation of PKS by Guo et al. (2005) by presenting high surface area on the PKS derived AC. The result showed that the C10 H_2SO_4 -PKSdAC-700 exhibited the highest impregnated Ba amount of 2.98 wt% from ICP-OES analysis, while XRF analysis indicates that C10 H_2SO_4 -PKSdAC-400 has the highest impregnated Ba on the surface at 35.46 wt%. The results indicated that large amount of Ba element was presented on the surface of PKSdAC than its interior when it was thermally treated at 400 °C, while the Ba amount on the surface of PKSdAC reduces compared to its interior when treated at 700 °C for using the same 10 % H_2SO_4 mass loading.

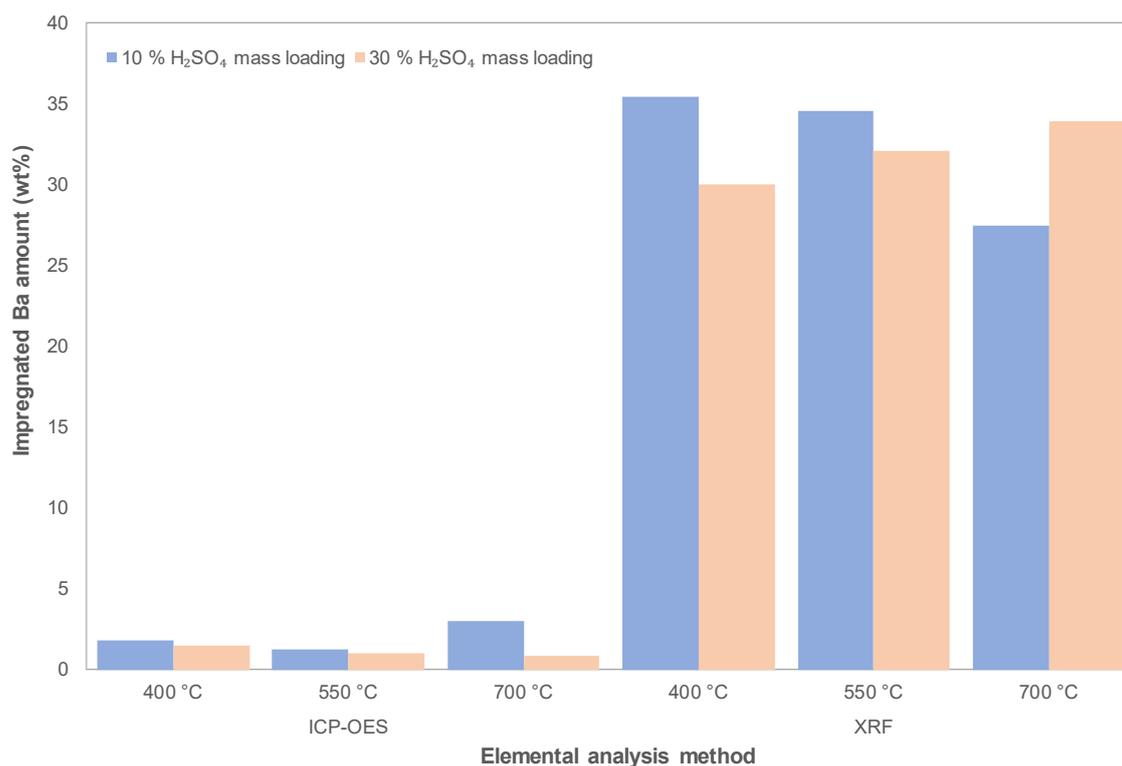


Figure 1: Effect of activation temperature on impregnated Ba amount in CAM-PKSdAC for different H_2SO_4 mass loading (10 % and 30 %) analyzed using ICP-OES and XRF

Activation temperature had a remarkable effect on the pore structure of PKSdAC, amount of carbon, and Ba produced in the derived PKSdAC. The mild-temperature activation at 400 °C and 550 °C produces less porosity and overage amount of carbon as reducing agent for reduction of BaSO_4 to barium sulphide (BaS) in producing Ba and leads to the reduction process shifted to higher temperature to occur, causing higher Ba amount impregnated on the surface of PKSdAC than in its interior pores (Balintova et al., 2017). In contrast to the mild-

temperature activation, high-temperature activation at 700 °C generates more porosity and lesser amount of carbon compared to mild-temperature activation to initiate the reduction process of BaSO₄ to produce Ba on the surface of PKSdAC and its interior pores. When the activation temperature increases, the impregnated Ba amount increases for 10 % H₂SO₄ mass loading, while it decreases at 30 % H₂SO₄ mass loading. The amount of Ba element impregnated on CAM-PKSdAC surface determined by XRF shows an opposite trend compared to the result from ICP-OES analysis. This manifests that the usage of 10 % H₂SO₄ mass loading favours the reduction of BaSO₄ in the presence of carbon derived from the carbonization of PKS at 400 °C to produce a high amount of Ba from barium sulphide (BaS) on the surface of PKSdAC (Balintova et al., 2017). In contrast, an increase in Ba amount was impregnated in its interior pores when it was heated at 700 °C (Hargreaves and Murray, 1989). This phenomenon showed opposite trends to 10 % H₂SO₄ mass loading when using 30 % H₂SO₄ mass loading in the preparation of PKSdAC due to overage amount of BaSO₄ formed that causes the reduction process of BaSO₄ shifted to high temperature and leading to lower Ba produced to impregnate into the pores and left unreacted BaSO₄ on the surface of PKSdAC.

To initiate the chemical adsorption of PKSdAC, formation of chemical bonding between CO₂ adsorbate and Ba metal salt in the interior pores of PKSdAC plays an important role. Incorporation of Ba into the PKSdAC interior is essential in the synthesis of activated carbon *via* CAM process. Comparing ICP-OES and XRF, ICP-OES is an analytical technique that is used as benchmarking tool to determine the appropriate activation temperature for CAM process in producing PKSdAC based on different H₂SO₄ mass loading. Unlike XRF, ICP-OES analyzed the total sample content from surface up to its interior and performed a sample dilution before the analysis to eliminate interferences from other chemical substances that may present in the sample which can alter the analysis result. It can be seen that CAM process that carried out at 700 °C using 10 % H₂SO₄ mass loading facilitate the absorption of Ba into the PKSdAC interior.

The result from Figure 1 showed that high Ba amount was detected by XRF analysis. This manifests that a relatively large amount of unreacted BaSO₄ salts which was formed from the reaction between H₂SO₄ presented on the surface of PKSdAC and BaCl₂ when soaking PKSdAC in the BaCl₂ solution was found on the surface after CAM process. This phenomenon can be observed from the SEM micrograph of C10H₂SO₄-PKSdAC-700 as shown in Figure 2 to 4 by showing a large amount of BaSO₄ salts presented on its surface than its interior pores as indicated with red square box in the micrograph.

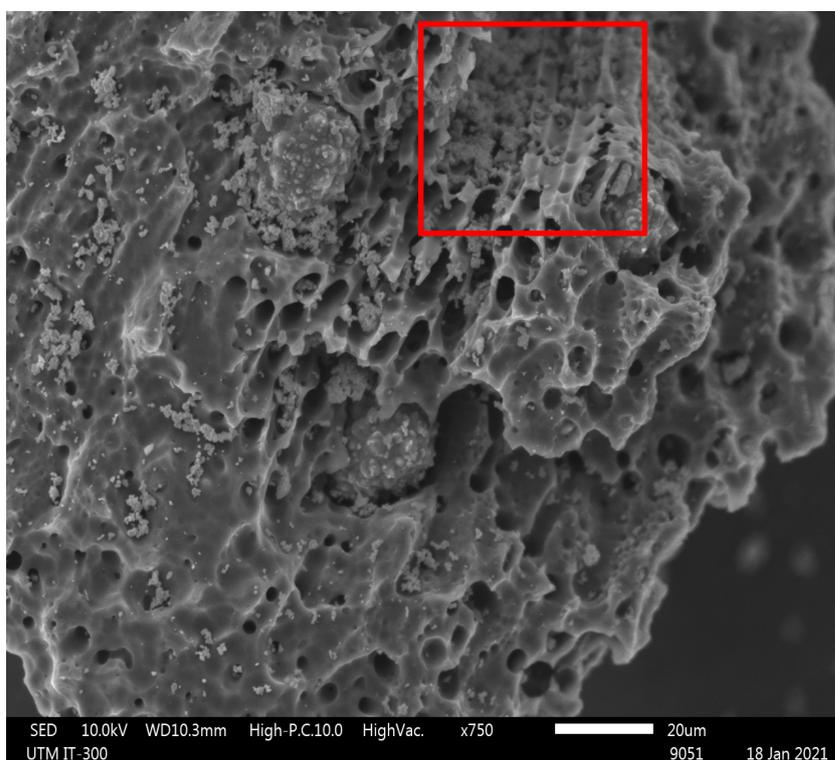


Figure 2: SEM images of CAM-PKSdAC (C10H₂SO₄-PKSdAC-700) by showing the structure of BaSO₄ salts at its surface after CAM process with magnification factors of 750

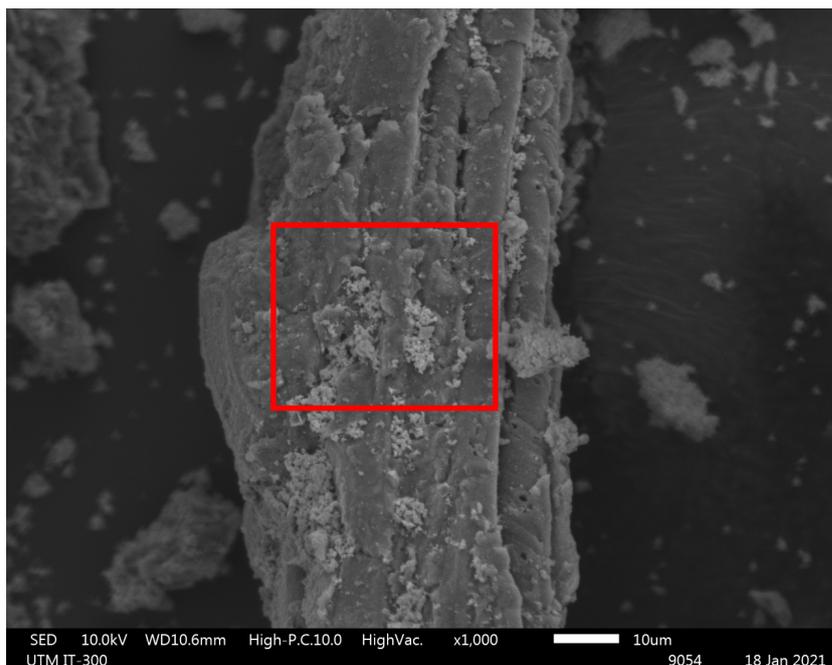


Figure 3: SEM images of CAM-PKSdAC ($C_{10}H_2SO_4$ -PKSdAC-700) by showing the structure of $BaSO_4$ salts at its surface after CAM process with magnification factors of 1,000

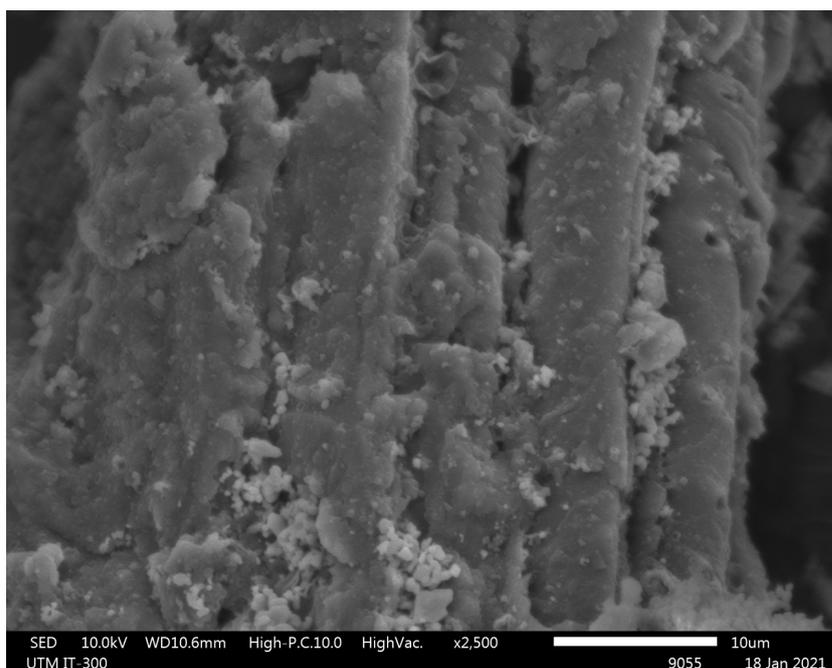


Figure 4: SEM images of CAM-PKSdAC ($C_{10}H_2SO_4$ -PKSdAC-700) with magnification factors of 2,500 by showing its surface and interior pores were occupied with $BaSO_4$ salts

4. Conclusions

A single-step concurrent activation and modification (CAM) process was performed to synthesize activated carbon (AC) from PKS. A parametric study on the synthesis of PKS derived AC (PKSdAC) by varying the H_2SO_4 mass loading and activation temperature manifests that the preparation of CAM-PKSdAC with 10 % H_2SO_4 mass loading resulted in a higher Ba amount impregnated from BaS produced from the reduction process of $BaSO_4$ on the surface of PKSdAC when it is heated at 400 °C, while on the contrary increasing Ba amount was

impregnated in its interior pores when it is heated at 700 °C. Incorporation of Ba metal salt in CAM-PKSdAC is essential for synthesis of activated carbon *via* CAM process. The derived activated carbon that prepared from CAM process is used as adsorbent to capture carbon dioxide (CO₂). The presence of Ba on the surface and interior pores of CAM-PKSdAC is dominant to initiate chemical adsorption of CO₂ by forming chemical bond between CO₂ adsorbate and Ba metal salt on the CAM-PKSdAC surface and pores.

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