ISSN (Print) : 0974-6846
Indian Journal of Science and Technology, *Vol 10(2), DOI: 10.17485/ijst/2017/v10i(2)/110377 January 2017* ISSN (Online) : 0974-5645

Impregnated Palm Kernel Shell Activated Carbon for CO_2 Adsorption by Pressure Swing Adsorption

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Abstract

Objectives: To study the application of impregnated palm kernel shell activated carbon (AC-PKS) as carbon dioxide (CO2) adsorbent for simulated coal-fired power flue gas. **Methods/Statistical Analysis:** The activated carbon was prepared using chemical (ZnCl2) activation method and impregnated with several types of metal oxides (Cerium, Barium and Titanium). The physico-chemical properties of PKS-ACs such as BET surface area, pore volume, and pore diameter were performed using N2 adsorption isotherm. Both loaded and unloaded ACs were also characterized using X-ray diffraction (XRD) and Scanning electron microscopy (SEM). The adsorption of CO2 from the simulated flue gas was investigated by pressure swing adsorption process in fixed-bed reactor. **Findings:** AC-PKS impregnated with Cerium Oxide (CeO2) showed the highest sorption capacity of CO2 among other impregnated metal oxides. AC-PKS/CeO2 also displayed the longest breakthrough time of 350 seconds for CO2 with 0.63 mole CO2/kg AC. The CO2 adsorption capacity of AC-PKS, AC-PKS-TiO2, PKS-AC/BaO and AC-PKS/CeO2 until complete saturation, were at 0.54 mole CO2/kg AC, 0.78 mole CO2/kg AC, 1.37 mole CO2/kg AC and 1.41 mole CO2/kg AC, respectively. During the desorption process, 99% of CO2 can be recovered and under 2 bar, 3 bar and 4 bar, the purity of CO2 was 25%, 36% and 38%. Interestingly, the purity increased to 93% when purging step with CO2 was added. **Application/Improvements:** This system will be implemented to capture CO2 from flue gas emissions from coal based power plant.

Keywords: Adsorption, CO2, Metal Oxides, Palm Kernel Shell Activated Carbon

1. Introduction

Fossil fuels including coal, petroleum and natural gas are the main sources of energy, producing a vast majority of fuel, electricity and heat used by people across the globe[1]. However, the burning of fossil fuels proportionally increases the carbon dioxide (CO_2) concentration into the atmosphere that has emerged as a significant environmental problem such as global warming[2]. Nonetheless, with the advancement of new technologies, for instance, the carbon capture and storage (CCS) the problem of CO_2 emission into the atmosphere can be mitigated[3].

Pressure swing adsorption (PSA) is the simplest way of capturing CO_2 from the flue gas stream mixture 4. However, it needs a suitable adsorbent for selective adsorption of CO_2 over other components in the flue gases, such as N2, NOx and SOx to ensure that the adsorption system can efficiently and economically enhanced the carbon capture system. During the adsorption process, CO_2 adsorbs into an adsorbent through physisorption or chemisorption mechanism based on the porosity and selectivity of the adsorbent5. CO_2 is then stripped off from the adsorbent during the desorption process, so that it can be regenerated. This process able to adsorb until 90% of CO_2 compared using biology method (microalgae) where their adsorption rate around 2.5 g/L6.

Activated carbon (AC) is known as the most effective adsorbents and widely used since most of its chemical and physical properties can be designed and adjusted according to the required applications[7]. Besides, the adsorption on activated carbon appears to be the most

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common techniques because of its simplicity of operation since the sorbents material can be made highly efficient, easy to handle and in some cases they can be regenerated[8].

AC also can be impregnated with variety of additives to enhance its adsorption performance and improve its selectivity. Impregnation of AC with selected metal oxide can improve its selectivity towards designated gas, whereby the metal oxide can influence the affinity of the AC. Impregnated AC can also accelerate the adsorption temperature and the process may takes place at lower temperature. Many types of metal oxides as AC impregnation agent have been studied, including Fe, Mn, Ce, Ni, V, Cu and Cr oxides in comparison to AC alone[9,10]. Researchers had reported that metal oxides i.e. CeO_2 supported over AC could capture both gases (SO_x and NO_x) simultaneously in a single step process. In[11] BaO has a high reactivity that enables it to donate charge to the adsorbed CO_2. Meanwhile, TiO_2 is a promising method for removing air pollutants.

The focus of this particular research project is on the capture of CO_2 from flue gases using activated carbon that was produced from biomass sources such as from mango seed shell, tapioca root, and palm oil[12,13]. In this study, palm kernel shell (PKS) since it is abundantly available in Malaysia and has very low market value. This paper presents the characteristics of PKS activated carbon as CO_2 adsorbent. Modification has been made by impregnating with metal oxide. Barium oxide (BaO), titanium oxide (TiO_2) and cerium oxide (CeO_2) onto the AC-PKS and adsorption and desorption study has been carried to observe their performance as CO_2 adsorbent.

2. Materials and Methods

2.1 Activated Carbon Preparation

PKS was mixed with $ZnCl_2$ solution with the ratio of 1:1 (mass basis) and was kept for about 24h at room temperature. The sample was then transferred into a stainless steel reactor as shown in Figure1 for activation. Nitrogen gas flow rate of 200 mL/min was used for making inert environment inside the reactor and removing the volatile compounds. The reactor was heated to 550°C and was kept at this temperature for about 1h.

Then, AC-PKS was loaded with 10wt% of selected metal oxide (BaO, TiO_2, CeO_2) to enhance the selective adsorption capacity of the adsorbent. This is due to these metal oxides have strong affinity towards CO_2. Initially, the solutions of chloride salts (reagent grade, 98% purity) of these metals were prepared in a beaker and a required amount of activated carbon was added into the solution. The mixture was left for 24 h at room temperature and was dried in oven for overnight. The dried sample was then placed in the same stainless steel reactor Figure1and was heated up to 750°C for 1 h under the flow of nitrogen gas.

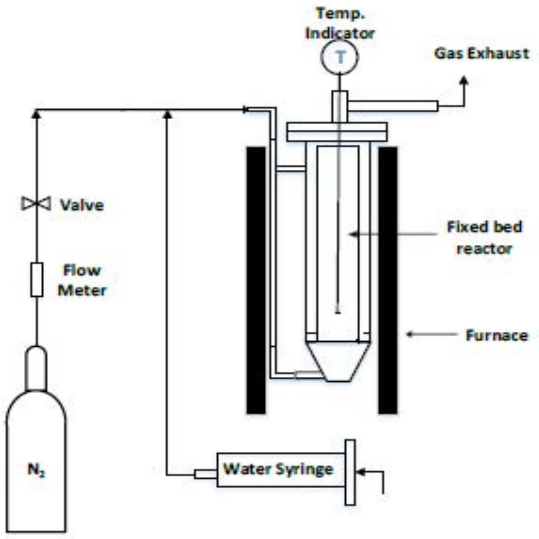


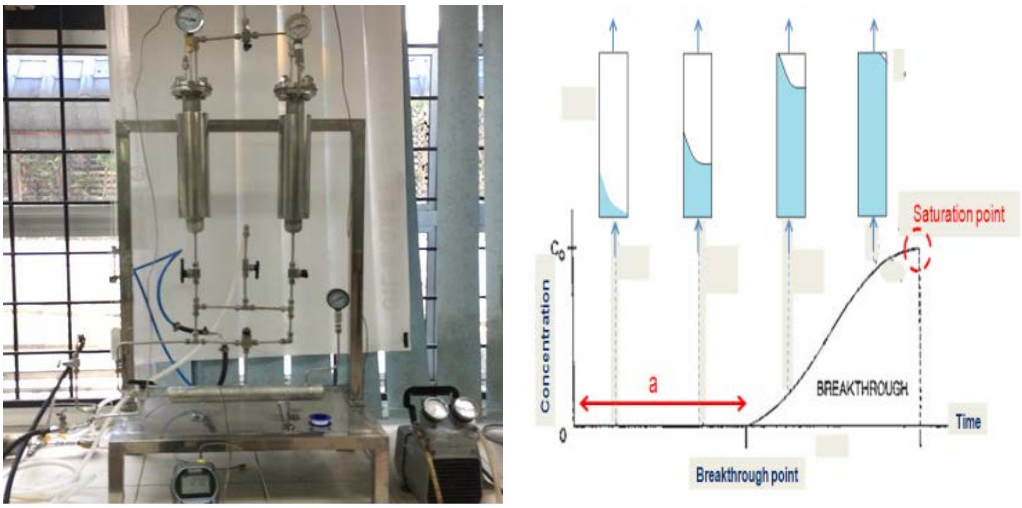
Figure 1. Experimental set-up for preparation of activated carbon.

2.2 Characterization

There are several characterization methods available to determine structural properties of porous adsorbents. In this study, all AC were characterized using BET surface area analyzer, X-ray diffraction (XRD) and Scanning electron microscopy (SEM) to facilitate the understanding of gas adsorption characteristics on the adsorbents.

2.3 CO_2 Adsorption-Desorption Process

The CO_2 adsorption test was carried out in a lab scale vacuum pressure swing adsorption (VPSA), as shown inFigure2a. For these experiments 10% of CO_2, 17 ppm SO_2, 20 ppm NO_2 and N_2 as a balance gas mixture were used. In each experiment 150g of adsorbent was used in the adsorption column, while 4 L/min of feed gas under NTP was passed until the saturation of adsorbent see Figure 2b. This study was monitored and recorded on an online portable gas analyzer (MRU Model OPTIMA 7,



(a) (b)

Figure 2. a)VPSA system b)illustration of breakthrough curve.

Germany).When the bed was fully saturated, the pressure was released and the adsorbed gas was recovered by means of vacuum and was collected in a gas bag.

3. Results and Discussion

3.1 Characterization of Activated Carbon

The BET surface area, pore volume and pore size for all samples including the impregnated samples were shown in Table 1. The BET surface area obtained was significantly high and it is within the acceptable range of commercial activated carbon (500-1500 m^2/g). Generally, with high BET surface area, results in higher adsorption capacity because the activated carbon is capable to adsorb more of gases under different conditions[14].

It can be observed that for chemical activated sample, PKS provided larger surface area which is1223 m^2/g. This is because the use of $ZnCl_2$ as the activating agent had contributed to the creation of more new pores and widen the existing pores. The pore volumes were determined from the isotherm and the PKS chemical activated carbon exhibited the highest pore volume (0.70 cm^3/g), which indicates higher gas adsorption.

However, when the ACs were loaded with metal oxide, the pore volume of the samples decreased. These observations indicate that the impregnation process allows the metal particles to be positioned in the most internal part of the pores, blocking the fine microporosity[9]. Consequently, pore volume for metal loaded was lower than the unloaded activated carbon. At this moment, adsorption of CO_2 was not only related to BET surface area and pore volume but also depended on reaction occurred between adsorbate (CO_2) and adsorbent (loaded AC).

Figure3 represents the spectrum of AC-PKS carbon and impregnated AC-PKS. From these figure, it can observed that AC-PKS exhibits two broad diffraction peaks located at 2θ = 20-30o and 40-50o that revealed the presence of amorphous structure which is disorderly stacked up by carbon rings and helpful for producing a well-defined adsorbent15. For the sharp peaks that were observed at 31.3o, 33.8o and 36.1o it could be due to the presence of ZnO species that was used during the chemical activation process.

The XRD pattern of modified ACs are slightly different where the two broad peaks were disappeared and substituted with additional peaks of metal oxide. It is also obvious that when other metal species is loaded on the AC-PKS, the Zn species phase is changed or covered by other metal layers like CeO_2, TiO_2 and BaO. Therefore, from XRD pattern is expected with highly dispersed metal species on activated carbon will improve the adsorption efficiency due to the chemisorptions that occurred between metal oxide and CO_2.

SEM technique was used to observe the surface physical morphology of the ACs. Figure4a shows the AC-PKS and Figure4b the impregnated AC-PKS. For AC-PKS, the surface is even more rough providing pores, channels, edge, peak and basal surface, which even contributed more to the BET surface area. When metal oxide was loaded on the ACs, the metal species

was homogenously distributed with nanometre range of particle sizes Figure 4b. Some of the metal species particles occupied the pores and channels; however, it also formed more edges and peaks on the basal surface. Ultimately the metal species loading provided more ability for gas adsorption[16].

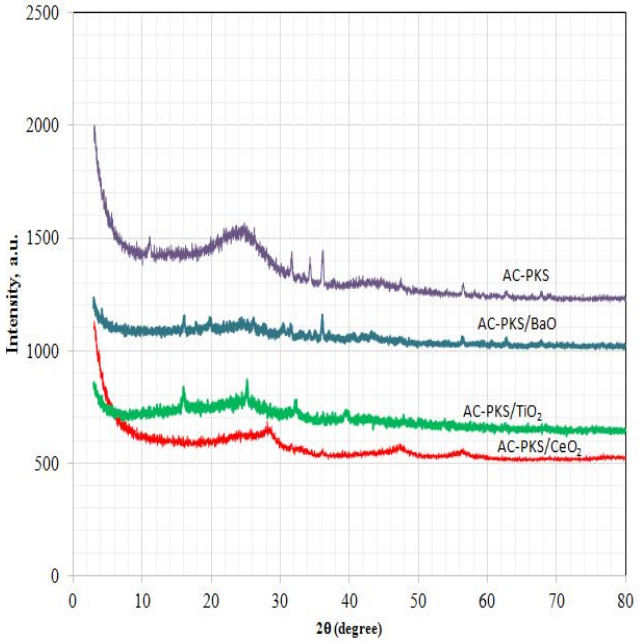


Figure 3. XRD pattern for AC-PKS and impregnated AC-PKS.

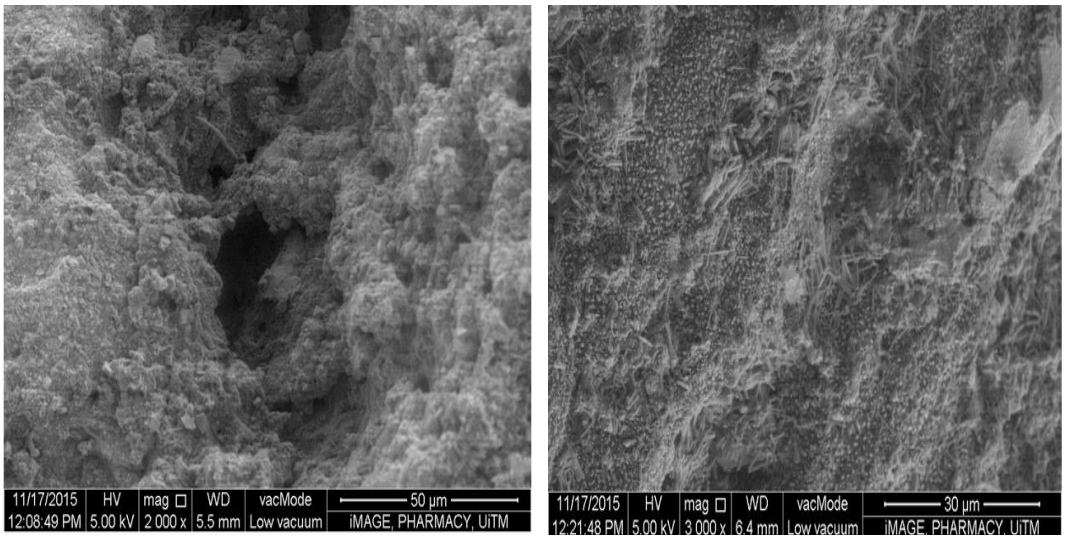
Table 1. BET Surface area

Sample	BET Surface area (m^2/g)	Total pore volume (cm^3/g)	Average pore diameter (Å)
AC- PKS	1223	0.70	22.88
AC-PKS/BaO	1250	0.67	21.50
AC-PKS/TiO_2	1170	0.50	17.17
AC-PKS/CeO_2	1125	0.65	21.24

3.2 Adsorption Breakthrough Curve

Figure 5 shows the breakthrough curves for AC-PKS, AC-PKS/TiO_2, AC-PKS/BaO and AC-PKS/CeO_2under 4bar pressure. A comparative study was done based on the breakthrough curves. The longer the sorbent could maintain 100% removal of CO_2 from the simulated flue gas, the better the prepared sorbent is. AC-PKS gave the lowest adsorption capacity of CO_2because of the shortest of breakthrough time. This is because virgin activated carbon only depends on the physisorption process. Whereas the impregnated ACs; AC-PKS/TiO_2, AC-PKS/BaO and AC-PKS/CeO_2 exhibits good result in adsorption of CO_2. The results show that the presence of metal oxide on the surface activated carbon increases the CO_2 adsorption efficiency. This is because CO_2 capture occurs chemically, through a chemisorption process[17]

From the figure, it was found that the best sorbent out



(a) (b)

Figure 4. SEM images of (a) AC-PKS and (b) modified AC-PKS (CeO2).

of three was cerium. AC-PKS/CeO_2 exhibits the longest breakthrough curve for CO_2 adsorption, 350 seconds and followed close by AC-PKS/BaO; 320 seconds, respectively. The poorest was AC-PKS/TiO_2 with 80 seconds, respectively. So, at this breakthrough point AC-PKS/TiO_2 could only adsorbed CO_2 at 0.15 moleCO_2/kg AC. Meanwhile, AC-PKS/BaO and AC-PKS/CeO_2 adsorbed0.58 moleCO_2/kg ACand 0.63moleCO_2/kg AC.The adsorption tests indicate that the higher breakthrough point value, the higher adsorption capacity.

Until complete saturation of the bed,0.54 moleCO_2/kg AC, 0.78 mole CO_2/kg AC, 1.37 mole CO_2/kg AC and 1.41 moleCO_2/kg AC were adsorbed on AC-PKS, AC-PKS/TiO_2, AC-PKS/BaO and AC-PKS/CeO_2,respectively. AC-PKS/CeO_2 showed the higher adsorption capacity of CO_2 than BaO and TiO_2. This is due, Ce has unique characteristics where it can give up oxygen atom without decomposing, release or take in oxygen. Therefore, CO_2 would get oxidized at the interface by oxygen from the support resulting high adsorption capacity of CO_2.

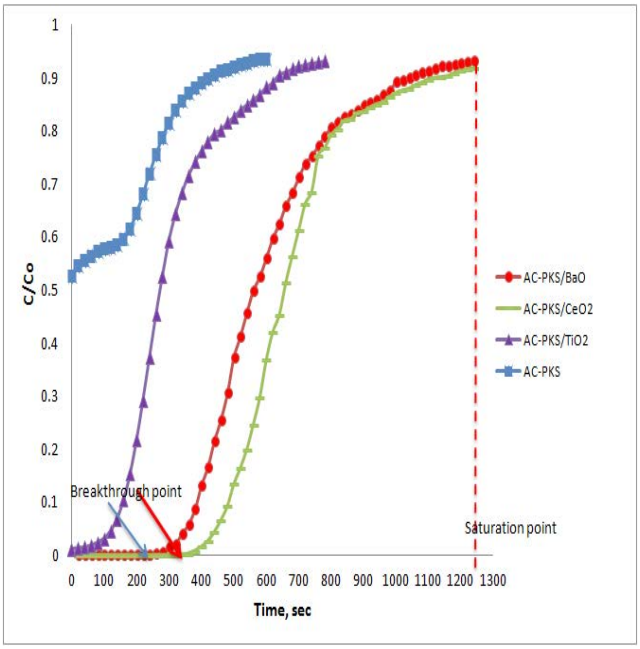


Figure 5. CO_2 adsorption breakthrough curves.

3.3 Recovery and Purity of CO_2 (Desorption)

The desorption (under vacuum) test indicate that AC-PKS/CeO_2 is the best adsorbent since it can recover 99% of the captured CO_2 and retained the most of SOx and NOx in the adsorbent Figure 6. Based on the acidity, SOx and NOx gases are more strongly bonded with metal loaded ACs surface. Under vacuum condition (P<1bar), CO_2 was desorbed and collected. Interestingly, the NOx and SOx did not desorbed. This is probably due to CeO_2could enhance the oxidation of NO to NO_2, NO_2 to NO_3 and SO_2 to SO_3 which indirectly assists to the highest simultaneously removal of NO_2 and SO_2. Furthermore, Ce could also develop the reduction of NO_2 to N_2[9].

The purity of the product gas depends on the adsorption pressure and purging step. The purging step was added because, after the breakthrough time, the bulk gas phase is nitrogen enriched gas. The purging with CO_2 from the bottom of the adsorber push out the nitrogen and the bulk phase is filled with CO_2. Without purging, under 2 bar, bar, 3 bar and 4 bar the purity was 25, 36 and 38%. When purging step with CO_2, the purity was increased to 93%. This step will helped to push out the nitrogen and make the bulk phase is filled with CO_2.

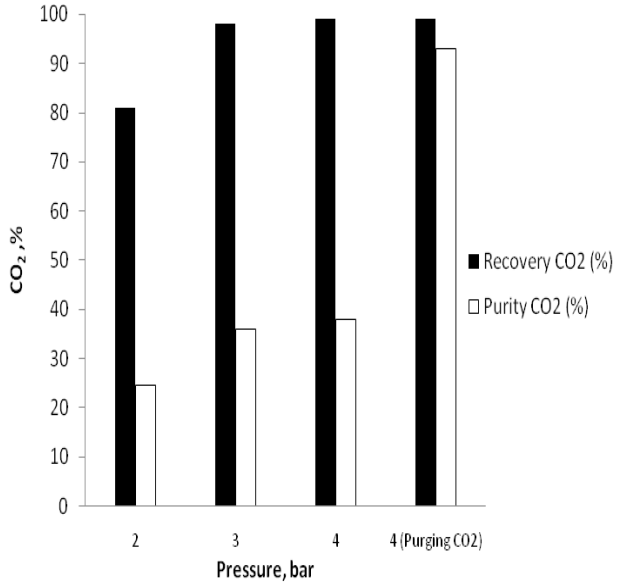


Figure 6. Recovery and purity of CO_2.

4. Conclusion

PKS can be used as the perfect raw material to prepare activated carbon with high surface area for CO_2 adsorption capacity. In addition, impregnated with metal oxide has increased the amount of CO_2 adsorption from the gas stream since it has the ability to form the strong interaction between metal oxides and CO_2.Among the prepared activated carbon, chemically activated PKS

impregnated with cerium oxide (CeO_2) shows a great adsorption of CO_2, 0.63moleCO_2/kg AC at breakthrough point and 1.41 moleCO_2/kg AC at saturation point in condition P=4 bar. In desorption process, 99% of CO_2 can be recovery and under 2 bar, 3 bar and 4 bar, the purity of CO_2 were increased and up to 93% when purging step with CO_2 was added.

5. Acknowledgement

This works was carried out with financial support from TNB Research Seeding Fund (R-C-SF-0238-16-011-1).

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