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Adsorption Isotherm Breakthrough Time of Acidic and Alkaline Gases on Treated Porous Synthesized KOH-$FeCl_3.6H_2O$ Sustainable Agro-Based Material

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Poisoning gases are very harmful when smelled and even low concentrations of the gases are can be lethal. The gases are widely used in various industries. Activated carbon (AC) can be useful to filter the gases. AC derived from local agricultural by-product materials can be used as adsorbent instead of using commercial activated carbon (CAC) for application in safety respiratory devices like gas masks. The study was carried out to produce AC derived from palm kernel shell (PKS) and to determine the breakthrough and saturation time adsorption isotherm of SO_2, NH_3 and O_2 on the AC produced. The preparation of AC involved two main steps which are carbonization and activation process. After carbonization process, the resulted char (PKS-char) was then impregnated with Potassium Hydroxide(KOH) and Ferric chloride hexahydrate ($FeCl_3.6H_2O$) followed by activation process using microwave heating. The prepared AC (PKAC-KOH-$FECl_3$) was characterized by Thermo-gravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR), Scanning electron microscopy (SEM) and Nitrogen adsorption isotherm. Breakthrough adsorption study was conducted in a stainless-steel reactor which loaded with 3.6 g of activated carbon for each run. The saturation time results were determined from the Yoon equation. From the adsorption breakthrough results, the PKAC-KOH-$FeCl_3$ produced 51 s, 100 s, and 6.33 s breakthrough time for SO_2, NH_3, and O_2 adsorption. The saturation time of PKAC-KOH-$FeCl_3$ for SO_2, NH_3, and O_2 adsorption were 16,947 s, 33,461 s, and 2,094 s. The results revealed that AC prepared from PKS treated with KOH-$FeCl_3$ can be further developed as potential adsorbent for the gas phase applications.

1. Introduction

Large amount of ammonia (NH_3) release will be hazardous and its toxicity can affect and give serious damage to the environment like photochemical smog formation and human health especially in the respiratory system (Bandosz and Petit, 2009). The National Research Council (NRC) concerned about NH_3 emissions which is a major air quality at global levels system (Bandosz and Petit, 2009). Sulfur dioxide (SO_2) has been identified as detrimental to human health. This issue brings to the development of SO_2 emission control technologies (Lee et al., 2002). Both of poisoning gases (NH_3 and SO_2) are widely used in various industries especially in chemical, oil and gas and petrochemical industry.

Palm oil has made impressive growth in the global market over the past four decades, and it is projected in the period 2016 – 2020, the average annual production of palm oil in Malaysia will reach 15.4 Mt (Hai, 2000). The production of palm oil in Malaysia increased to 18.8 Mt in 2012 since 1985 which is about 4 Mt (Chang, 2014).

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Oil palm industries produced abundant amount of palm wastes. If this waste not managed properly in disposal process, it will give environmental problem. About 90% of the oil palm trees are regarded as waste and the remaining is oil. The alternative of converting low value of palm biomass wastes into high value-added product like activated carbon can effectively reduce the environmental impact which is caused by unscientific manner of incineration the palm wastes (Nizamuddin et al., 2016). The production of activated carbon using agro-waste materials have been proven as promising and interesting method due to their availability at a low price. The raw materials can be used as precursor for the production of activated carbon based on their considerable mechanical strength, low ash content and high adsorption capacity (Nizamuddin et al., 2016).

Nowadays, there are many waste management techniques which can be employed to deal with the waste such as pyrolysis and gasification technique. The waste will be handled at very high temperature and high pressure by using these thermal techniques. For example, in pyrolysis process, the waste substance is transformed to solid or liquid. Pyrolysis is the most promising thermal conversion and low-cost process among the processes of energy production from biomass. The bio-char production from slow pyrolysis is the process with most positive environmental impact and enhances the quality of char.

Mostly the activated carbons are produced through two-step physical activation followed by one-step chemical activation. The two-step physical activation involved pyrolysis of the raw material or precursors and proceed with activation using CO_2, steam or air. The one-step chemical activation involves treatment with chemical agents in inert atmosphere including potassium hydroxide (KOH), sulphuric acid, zinc chloride and many others.in (Wu et al., 2013). For the present work, the entire adsorbent material acts as the filtration media of respiratory separation of adsorbents to provide protection against acute and chronic adverse health effects from an excessive contaminated air during work. This application is special case in gas mask application. Many work done using palm kernel shell activated carbon (PKS-AC) as adsorbent for gas adsorption but in different field like gas storage. The using of Ferric chloride hexahydrate ($FeCl_3.6H_2O$) as second chemical treatment on the adsorbent surface is the new approach to enhance the gas capturing properties. The microwave heating used is technology used to improve the surface properties.

For the present study, the raw palm kernel shell material undergoes pyrolysis process first to produce bio-char and then was impregnated with KOH and $FeCl_3.6H_2O$. The impregnated-char then was activated using microwave heating. The objectives of this study were to synthesize activated carbon from agricultural waste material (PKS) and to determine the adsorbent performances for adsorption breakthrough of the poisoning gases (SO_2 and NH_3) on the PKS-activated carbon. This scope of research attempted to study the adsorption of SO_2, NH_3 and O_2 in the fixed bed of activated carbon as a means to treat its emissions via gas mask application. The present work aims to determine the breakthrough time of the gases adsorption and evaluate the saturation time using selected mathematical model.

2. Methodology

2.1 Material preparation

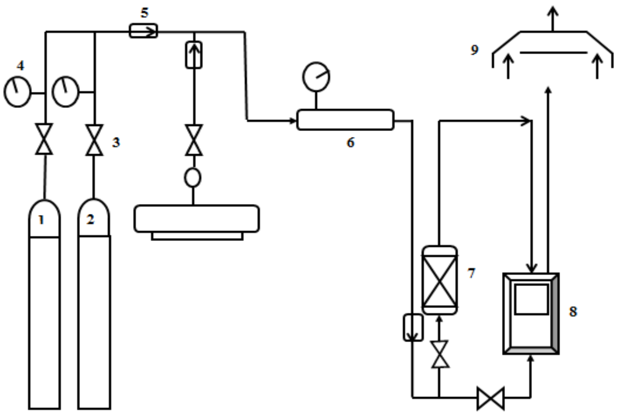
Precursors PKS was pre-treated by manual cleaning, dehydration under sunlight for 6 h, washed with deionized water until reached pH 6.5 - 7 and then drying in oven for 24 h at 105 °C. The raw material (PKS) was carbonized at a rate of 10 °C /min from room temperature to 700 °C at 150 mL/min flow rate of nitrogen. It was held at that temperature for 2 h before cooled down to room temperature under nitrogen flow (Nasri et al., 2014). Palm kernel chars were sieved in the range size of 0.6 - 0.85 mm and followed by chemical surface modification. The impregnation of the chars involved potassium hydroxide (KOH) first and then treatment with ferric chloride hexahydrate ($FECl_3.6H_20$). PKS chars were mixed with 2M of KOH solution with 1:1 ratio by weight. After that, the mixture of chars and KOH solution was heated at 85 °C and speed 6 r.p.m and then dried in oven at 105 °C for 24 h. Then, the PKC-KOH was impregnated with $FECl_3.6H_20$ with 1:5 ratios**.** The conditions for this heating process same with PKC-KOH preparation which was at 85 °C and speed 6 r.p.m. Activation process was done with 200 ml/min N_2 for 10 m duration and then switched over to 200 ml/min CO_2, 400 W microwave power level for 10 m irradiation time (Nasri et al., 2014).

2.2 Material Characterization

The thermal decomposition properties of the palm kernel shell were studied using TG analysis with thermo gravimetric analyser (Mettler Toledo TGA/DSC1). Perkin Elmer FTIR spectrometer was used to analyse the functional groups presence in the activated carbon. The FTIR results of the activated carbon provide a quick and simple qualitative technique (Nasri et al., 2014). The absorption range was recorded from 4,000 to 400 cm^{-1}. SEM analysis was observed using Karl Zeiss (Evo50 XVPSEM, Germany). It was used to study the growth and development of pores on the surfaces of adsorbents due to thermal and chemical treatments. Micrometrics ASAP 2020 equipment was used to determine the surface area and pore structure of the sample. Brunauer, Emmett and Teller (BET) evaluated the surface area from the adsorption data in the relative pressure (P/P_0) range of 0.04-0.2.

2.3 Single adsorption and breakthrough study

The adsorption unit was used to monitor the breakthrough curves for three type of single gas; sulphur dioxide (SO_2), ammonia (NH_3) and oxygen (O_2). The gas cylinder directly connected to the test rig. The initial reading of concentration SO_2 was taken first. Then proceed to the adsorption step in which the gas was fed through the column. The feed gas inlet concentration was set at 100 mL/min. Breakthrough time adsorption experiments were carried out at 10 ppm of SO_2 and NH_3.The single gas breakthrough adsorption was conducted in the fume cupboard with 1m/s face velocity. Gas analyser (MSA) was used to determine the gas effluent concentration breakthrough time. The breakthrough time adsorption was taken when the gas analyser just detected the gas effluent concentration. The experiment was repeated for 3 different samples to have an average breakthrough time results of SO_2, NH_3 and O_2 with each 3.6 g of sample (Garcia et al., 2011).



1. Carrier Gas Cylinder (Air/N_2), 2. Poisonous gas cylinder, 3. Check valve, 4. Pressure Indicator, 5. Volumetric flow meter, 6. Loading Cell/Gas Mixer, 7. Fixed bed adsorption cell, 8. Gas Detector, 9. Scrubber Fume cupboard.

Figure 1: Schematic diagram of the column breakthrough experiment

The breakthrough behaviour of the gases on fixed bed adsorbent was studied theoretically using the Yoon equation in establishing a relationship between the theoretical time, equilibrium sorption capacity and the gas concentration changes due to adsorption. Details of the mathematical model and its usage in evaluating breakthrough adsorption can be found elsewhere in Zain et al. (2016).

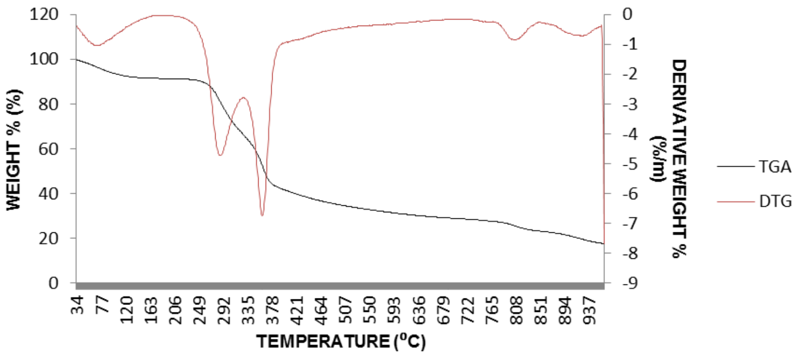


Figure 2: TGA-DTG analysis on palm kernel shell

3. Results and discussions

3.1 Characterization results

The DTG/TGA thermal analysis on the PKS material was carried out in order to know the suitable heating temperature for the carbonization process. Basically, the weight loss and thermal decomposition during the TG analysis of the materials are divided into three stages namely, drying and evaporation, de-volatilization (hemicellulose and cellulose decomposition) and lignin decomposition. From the result obtained, at temperature 30 ˚C to 60 ˚C, materials mass loss was detected which could be due to vaporization of physically adsorbed water (Yin et al., 2007). The TGA curve remain constant and stable at temperature 600 ˚C to 800 ˚C due to no longer weight loss and the completion of all the waste materials decomposition. The materials cannot burn anymore and achieved stable temperature region.

Figure 3 observed the SEM image of raw palm kernel shell (PKS), palm kernel char (PKC) and palm kernel activated carbon treated with KOH and FeCl3 (PKAC-KOH-FeCl3). The cellular structure was observed in SEM image of PKS (Figure 3a) which commonly observed from ligno-cellulosic materials and carbonaceous materials (Nasri et al., 2014). Some pores were observed on the surface of PKC (Figure 3b). The pores were created during carbonization process and become increasing and widening after activation process.
A coarse surface was observed on SEM image of PKAC-KOH-FeCl3 (Figure 3c). Some chemical agents constituent particles distributed on the surface of PKAC-KOH-FeCl3.Similar observation have been reported in Tsai et al. (2001) and Choo et al. (2013) SEM results for their report observed that NaOH and K2CO3 crystal distributed on the activated carbon. In this study, it was observed that KOH and FeCl3 form caused only minor pore blockage. This is due to the washing process with distilled water was applied after activation process so that some impurities have been removed. These salts could be pushed out of the cavities by washing the product with 0.1M HCl.

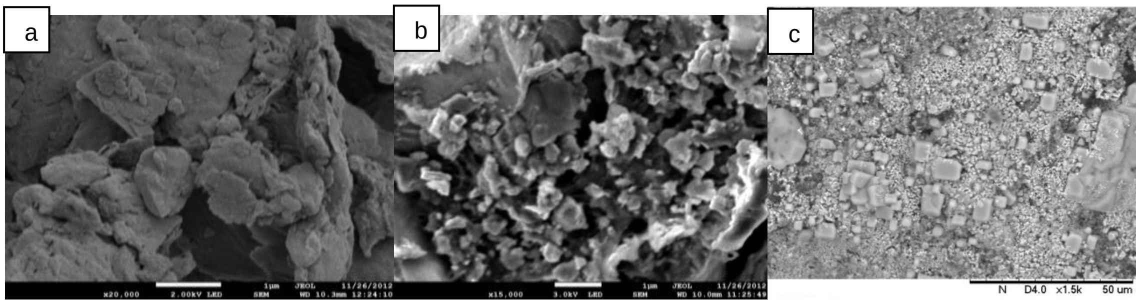


Figure 3: SEM image of a) Raw PKS b) PKC c) PKAC-KOH-$FeCl_3$

Table 1: BET surface area, total pore volume and average pore size of PKC and PKAC-KOH-$FeCl_3$.

Sample	BET surface area (m^2/g)	Total pore volume (cm^3/g)	Average Pore Size (nm)
PKC	24.50	0.01517	2.477
PKAC-KOH-$FeCl_3$	122.61	0.06205	2.194

Table 2: Summary table for peak wave number Palm Kernel Activated Carbon-KOH-$FeCl_3$

Wave number range (cm^{-1})	Peak wave (cm^{-1})	Group	Compound
3,600 - 3,300	3,435.53	O-H	Phenols, alcohols
1,680 - 1,640	1,637.44	C=C	Alkenes
1,750 - 1,630	1,685.10	C=O	Carbonyl (amide, ketone, aldehyde)
850-550	550.60	C-Cl	Alkyl halide

Table 3: Breakthrough time for 3.6 g of activated carbon (experiment)

Sample	Breakthrough time(s) (exp.)
SO_2	51
NH_3	100
O_2	6.33

The specific surface area and total pore volume of PKAC-KOH-$FeCl_3$ was higher compared to that of palm kernel char as presented in Table 1. The results obtained showed that the surface area and pore volume of the PKAC-KOH-$FeCl_3$ increased after undergo the activation process. During the activation process, carbon dioxide diffused through the materials and essential in enhancing the pores on the materials.
The first peak wave of PKAC-KOH-$FeCl_3$ was found at 3,435.53 cm^{-1} which belonging to phenols and alcohol groups. Alkene, aliphatic amines, and carbonyl groups also appeared in FT-IR spectrum of PKAC-KOH-$FeCl_3$. The presence of alkene group on the surface of activated carbon materials suggested as the characteristics of cellulose and hemicellulose (Chingombe et al., 2005). The vibration between 850 and 550 cm^{-1} presented on PKAC-KOH-$FeCl_3$ are assigned to alkyl halides group and it could be due to the presence of chloride. The

common functional groups like carbonyl and alkene also presented on FT-IR spectrum of PKAC-KOH-$FeCl_3$ material.

3.2 Single gas adsorption in breakthrough study

3.2.1 Breakthrough time of single gas adsorption

The result for the adsorption isotherm breakthrough time of acidic and alkaline gases was presented in Table 3. PKAC-KOH-$FeCl_3$ recorded 51 s, 100 s and 6.33 s breakthrough time for the SO_2, NH_3 and O_2 adsorption respectively. PKAC-KOH-$FeCl_3$ has magnetic properties with attracted the gas molecules (Mubarak et al., 2014). The treatment with $FECl_3.6H_20$ is a second treatment used to enhance the ability of the surface adsorbent in gas capturing properties. The lower breakthrough time produced for the gases adsorption might be due to the low feed concentration used which is 10 ppm that reduced the driving force along the pores of the sample (Xiao et al., 2008). PKAC-KOH-$FeCl_3$ produced the longest breakthrough time in NH_3 adsorption might be due to the strong molecules interaction of the adsorbent and NH_3 and the performance also depend on properties of the gas. The bonding between the PKAC-KOH-$FeCl_3$ and SO_2 could be not as strong as the bonding between PKAC-KOH-$FeCl_3$ and NH_3. Oxygen adsorption testing was used as a requirement for the human breathing. PKAC-KOH- $FeCl_3$ produced shorter breakthrough time in O_2 adsorption and it is good to be used for the gas mask respirator.

3.2.2 Saturation time of single gas adsorption

The saturation time of SO_2, NH_3 and O_2 adsorption on the sample was presented in Figure 4 and Table 4. The saturation time was determined using Yoon equation. Saturation time means that the gas concentration achieved above 90-95 % of breakthrough adsorption (SEA, 1997). The saturation time cannot be achieved in the experimental study due to the limited gas and long-time is needed in order to achieve the saturation level. PKAC-KOH-$FeCl_3$ recorded 16,947 s, 33,461 s and 2,094 s of saturation time for SO_2, NH_3 and O_2 respectively. The trend of the results obtained for the saturation time was same with those results obtained from the breakthrough time. The Yoon equation can be a suitable method in determining the breakthrough and saturation time. From the saturation time result, the PKAC-KOH-$FeCl_3$ produced the longest saturation time in NH_3 adsorption. This shows that the sample have a higher capability of adsorbing NH_3 which makes it easier for the gas to fill-up their pores. The gas capturing of NH_3 was enhanced by second treatment with $FeCl_3$ which having magnetic properties. The sample would be more suitable in NH_3 adsorption. Generally, same with breakthrough time results, the results for the saturation time in adsorption of oxygen for the sample also the shortest one. This short period taken indicated that the sample was not attracted to the oxygen and that enabled it to be easily filtered. This result was good in air breathing and gas mask respirator.

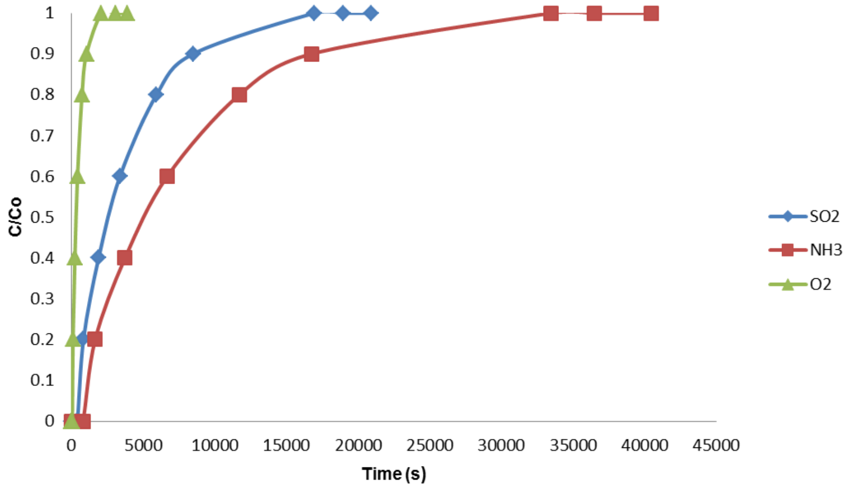


Figure 4: Saturation time for SO2, NH3 and O2 adsorption

Table 4: Saturation time for 3.6 g of activated carbon (calculation)

Gas	Saturation time(s)
SO_2	16, 947
NH_3	33, 461
O_2	2, 094

4. Conclusions

The breakthrough time of SO_2, NH_3 and O_2 adsorption on the PKAC-KOH-$FECl_3$ were obtained at 51 s, 100 s and 6.33 s. The PKAC-KOH-$FECl_3$ sorbent recorded the longest breakthrough time in NH_3 adsorption at 100 mL/min inlet flow rate. The adsorption breakthrough experimental data compared with the data obtained from Yoon equation and the equation applicable to be used in determining of saturation time. The adsorbent produced from palm kernel shell can be a potential product to be applied further in gas mask respiratory system based on the good results in characterization and adsorption breakthrough study.

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