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Sulphur Dioxide and Oxygen Adsorption Isotherm Breakthrough Time on Surface Porous Palm Shell Activated Carbon

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Sulphur dioxide (SO_2) releases from various industries can affect the environment and human health. Activated carbon has been widely studied in gas and liquid adsorption due to its capability in filtration to remove organic materials and particulate matter. Palm kernel shell (PKS) is an agricultural by-product from palm-oil processing mills. PKS has been used as the based material for the production of activated carbon (AC). The research is aimed to produce AC derived from sustainable palm solid waste and to study the breakthrough time adsorption isotherm of SO_2 and oxygen (O_2) on the AC. In this study, palm kernel shell activated carbon (PKS-AC) was prepared via carbonisation, impregnation and activation. The dry PKS was carbonised at 700 °C for 2 h in a furnace and was then impregnated with ferric chloride hexahydrate ($FECl_3.6H_2O$) in 1 : 5 ratios (ferric chloride hexahydrate to PKS-char). The treated PKS-char was activated through microwave heating at 400 W power level and 6 min irradiation time. The prepared AC were characterised using Thermo-gravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR), Scanning electron microscopy (SEM) and Nitrogen adsorption isotherm. Breakthrough adsorption of SO_2 and O_2 was investigated in a fixed-bed reactor. The results shows that the prepared AC produced 23 and 7.5 s breakthrough time for SO_2 and O_2 adsorption. In conclusion, AC that produced from agricultural waste via impregnation with ferric chloride and microwave induced can be a new promising method for the production of simple and good quality of AC.

1. Introduction

SO_2 is emitted mainly from industry activities like refineries, petrochemicals facilities and desulphurisation. This gas can affect the human health and environment at certain concentration. In order to overcome this problem, the safety respiratory devices like gas masks have been applied via adsorption technology. However, the available gas mask uses commercial activated carbon which is mainly derived from coal. Coal is non-renewable materials and very expensive compared to renewable sources like agricultural wastes. Activated carbon derived from local agricultural biomass is cheaper than other adsorbents like silica, zeolite and alumina. Nowadays, much research focus on synthesising activated carbon (AC) from sustainable agro waste materials like palm kernel (Hamza et al., 2015), empty fruit bunch (Foo and Hameed, 2011) and

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coconut shell (Mohammed et al., 2015) which are low cost, renewable and abundantly available. It is widely used for the adsorption of harmful gas at low concentration because of its high specific area and extremely porous structure (Adinata et al., 2007). The removal of liquid and gas using adsorption method become widely popular especially using AC as adsorbent. This is due to its advantages like low cost operation, good potential in air pollution control, simple and efficient method (Auta and Hameed, 2013). There are few number of studies that have been reported for adsorption of SO_2 and all the report used commercial AC as adsorbent. Commercial activated carbon adsorption behaviour for SO_2 was reported previously by Zhang et al. (2007).
AC can be produced with different carbonising and activating conditions which depend on biomass's properties (Choo et al., 2013). Commonly the precursor is carbonised first under nitrogen gas with conventional heating via electric furnace and then impregnated with an activating agent, such as $ZnCl_2$, H_3PO_4 and KOH followed by activation process with carbon dioxide. Microwave heating is currently used in activation process because it can reduce the treatment time considerably and energy consumption (Foo and Hameed, 2009). In this study, AC was derived from agricultural waste material i.e. Palm kernel shell through carbonisation process followed by impregnating with Ferric chloride hexahydrate ($FECl_3.6H_2O$). The impregnated PKS was activated by microwave heating technique to produce PKS activated carbon. The performance of the produced activated carbon was applied to adsorb SO_2 and O_2 gases through adsorption breakthrough study. This study was also carried out to get better understanding of the adsorbent's characteristics for the gas adsorption process.

2. Methodology

2.1 Material preparation

PKS was used as precursor for the preparation of the activated carbon. The dry PKS was carbonised at 700 °C for about 2 h in a furnace before cooled to room temperature. Palm kernel char was treated with Ferric chloride hexahydrate ($FECl_3.6H_2O$) in the ratio 5 : 1. 10 g of $FECl_3.6H_2O$ mixed with 50 g of palm kernel char in 30 mL deionised water (Mubarak et al., 2014). Then, the mixture of chars and Ferric chloride hexahydrate solution was stirred at 6 rpm using magnetic stirrer and was heated at 85 °C. For the activation process, Impregnated palm kernel char (PKC-$FECl_3.6H_2O$) was activated using microwave heating. 30 g of PKC-$FECl_3.6H_2O$ was put into a quartz reactor. The sample was pre-heated in microwave oven with 200 mL/min flow rate of nitrogen gas. The flow was then switched over to carbon dioxide gas which flow rate at 200 mL/min. The power level was used at 400 W from power controller with 10 m of irradiation time (Hamza et al., 2015). The resulting activated carbon was labelled as PKAC-$FeCl_3$.

2.2 Material Characterisation

The characterisation of the sample for this study involved chemical and physical method. The surface chemistry and functional groups of the sample was identified using Perkin Elmer Fourier Transform Infrared Spectroscopy (FTIR) spectrometer. The IR spectrums describe the functional groups, chemical bonds, wavenumber of the peaks and the type of vibrations. The absorption range was recorded from 4,000 to 400 cm^{-1}. Scanning Electron Microscope (SEM) examination was carried out for the samples by using Karl Zeiss (Evo50 XVPSEM, Germany). SEM was used to observe the development of porosity of the sample (Mohammed et al., 2015). The surface area and pore structure of the adsorbent were analysed by liquid nitrogen adsorption at -196 °C using Micrometrics ASAP 2020 equipment. This technique was carried out to obtain adsorption isotherms, which then used to get the surface area. Brunauer, Emmett and Teller (BET) theory was used to determine the specific surface area through gas adsorption measurement. This method was used to characterise the structural aspects of the porosity which is based on the interpretation adsorption isotherm (Din et al., 2009).

2.3 Single adsorption and breakthrough study

Adsorption breakthrough data was obtained in a stainless-steel fixed-bed reactor. About 3.6 g of adsorbent was used for each run. In a breakthrough experiment, SO_2 gas was flowed first before it contacted with adsorbent while valve of adsorption cell remains closed. The feed gas inlet concentration was set at 100 mL/min. The initial reading of concentration SO_2 was taken. Then proceed to the adsorption breakthrough step in which SO_2 gas was fed through the column. The valve located between the mass flow meter and adsorption cell was opened to enable the gas contact to the adsorbent. For detection of the compositions of reacted samples, gas analyser was set up to the inlet and outlet stream of reactor. The concentration was recorded from first point of SO_2 detected in the effluent (Sumathi et al., 2010). The experiment was repeated for O_2 with another 3.6 g of sample.

2.4 Simulation breakthrough study

A mathematical model is created mainly to study characteristics of the breakthrough for adsorbent in the adsorption column and to determine the key working parameters for controlling the adsorption process. Many type of mathematical model have been proposed in order to estimate the breakthrough equation theoretically. In this study, Yoon equation was used for determination of breakthrough time (theory) and the results are compared to the breakthrough time (actual) results obtained from experiment. Yoon equation is the derivation from Mecklenburg and Wheeler equation. Yoon has developed less complicated models compared to others (Aksu and Gonen, 2004). This equation is almost similar to the Wheeler equation but it is arranged in different way to get another shape of the breakthrough curve at high concentration (SEA, 1997). The breakthrough time of the single gas adsorption on PKAC-$FeCl_3$ is calculated using the following equation:

$$k_v = 14.4 \left(\frac{1{,}000Q}{nA}\right)^{1/2} d^{-3/2} \quad (1)$$

According to Eq(1), k_v represents the adsorption rate constant (min^{-1}), Q is the inlet flow rate of single gas (cm^3/min), n is the number of filter used during testing and A is the cross-sectional area of carbon bed (cm^2).

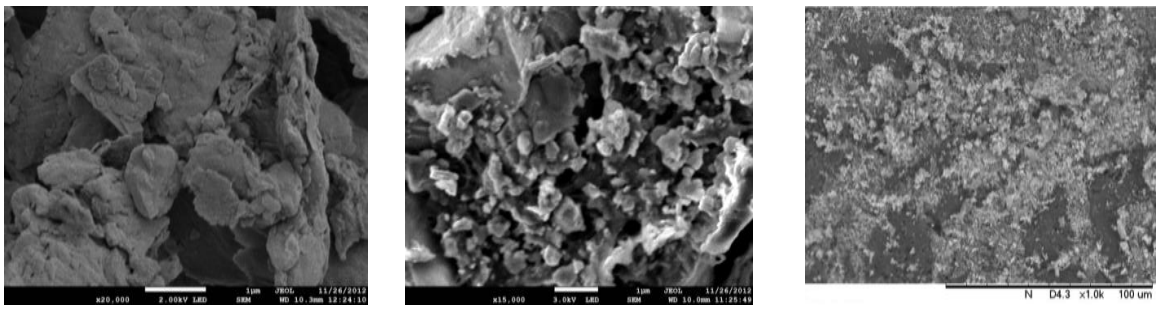
$$t_\beta = \frac{W_e}{C_o \times 1{,}000Q} \times \left[W - \frac{\rho \times c \times 1{,}000Q}{k_v}\right] \times \ln\left(\frac{C_i - C}{C}\right) \quad (2)$$

Where, W_e is the adsorption capacity (g/g), ρ_c is the carbon density (g/cm^3), W_c is the total weight of carbon used inside the bed (g), C_i is the Inlet concentration (ppm), C_o is inlet concentration (g/cm^3), C is the breakthrough concentration, M is the molecular weight of the adsorbent (g/mol) and d is diameter of carbon bed (cm), t_β is breakthrough time (min) These data are needed to solve the Yoon equation (SEA, 1997).

3. Results and discussions

3.1 Characterisation results

Figure 1 shows the surface morphologies of raw palm kernel shell (PKS), palm kernel char (PKC) and palm kernel activated carbon treated with $FeCl_3$ (PKAC- $FeCl_3$). SEM image of PKS (Figure 1(a)) shows a cellular structure which commonly observed from lignocellulosic materials (Nasri et al., 2014). Surface with small pores is observed on the PKC (Figure 1(b)). The pores observed are restricted. The pores were created during carbonisation process. The pores become increasing and widening as a result of impregnation with $FeCl_3$ and activation with CO_2. At this process, the moisture and other impurities were volatilised (Mohammed et al., 2015). SEM result of PKAC-$FeCl_3$ (Figure 1(c)) shows the present of cavities over the surface of PKAC-$FeCl_3$ and pore network.



(a) (b) (c)

Figure 1: SEM image of (a) raw PKS, (b) PKC, (c) PKAC-$FeCl_3$

The results of BET surface area and porosity for PKC and PKAC-$FeCl_3$ are presented in Table 1. The specific surface area of PKAC-$FeCl_3$ is higher compared to that of the PKC. It could be because of $FeCl_3$ has been impregnated into pores of PKC. The surface area is important property of activated carbon which significantly influenced the adsorption performance (Choo et al., 2013). Activation process enhances the development of porosity in the material. During the activation process, carbon dioxide diffused through the materials,essential in enhancing the pores on the materials. PKAC-$FeCl_3$ contained 73.43 % pore volume of the total pore volume. The low BET surface area obtained might be affected from the production of inhibitor during activation (Rugayah et al., 2014) or might be due to blockage of cavities. From the results obtained, it shows that the surface area and pore volume of the PKAC-$FeCl_3$ increased after activation.

Table 1: BET surface area, Pore volume, Total pore volume and Average pore size of PKC and PKAC-$FeCl_3$.

Sample	BET surface area (m^2/g)	Volume in pore (cm^3/g)	Total pore volume (cm^3/g)	Average Pore Size (nm)
PKC	24.50	0.008686	0.01517	2.477
PKAC-$FeCl_3$	75.0067	0.02714	0.03696	2.13788

From Figure 2, it is noticed that the FT-IR spectrum shows the presence of some peaks which belonging to functional group such as alkanes, alkenes, alkyl halides and hydroxyl. The spectrum of the samples (Figure 2) displays the bands between 3,200 and 3,600 cm^{-1} which attributed to the O-H stretch in alcohols (Liu et al., 2010). The spectra also shows the bands between 1,600 - 1,400 cm^{-1} which correspond to C=C stretch aromatics and presents the peaks between 1,300 – 1,000 cm^{-1} that related to C-O groups (Nasri et al., 2014). The presence of alkene group on the surface of palm kernel shell activated carbon suggests as the characteristics of cellulose and hemicellulose (Chingombe et al., 2005). However, the FT-IR spectra of PKC shows some differences from that of the PKS and PKAC-$FeCl_3$. The spectrum presents the following bands, 1,250 - 1,120 cm^{-1} which refers to C-C-C stretch in di-alkyl group and 1,750 - 1,735 cm^{-1} which are assigned to C=O ethers (Nasri et al., 2014). From Figure 2(c), the vibration between 850 and 550 cm^{-1} presented on PKAC-$FeCl_3$ is assigned to alkyl halides group and it could be due to the presence of chloride. The strong absorption peak is observed at 1,309.51 cm^{-1} which is assigned to C-O structures. The peaks at wave numbers of 2,890.01 cm^{-1} corresponds to the funtional group of C-H stretching (Wade, 2010). The spectra of PKC also presents the band at 2,850 - 3,000 cm^{-1} which refers to C-H stretch in alkane that same with the band presented for spectra of PKAC- $FeCl_3$.

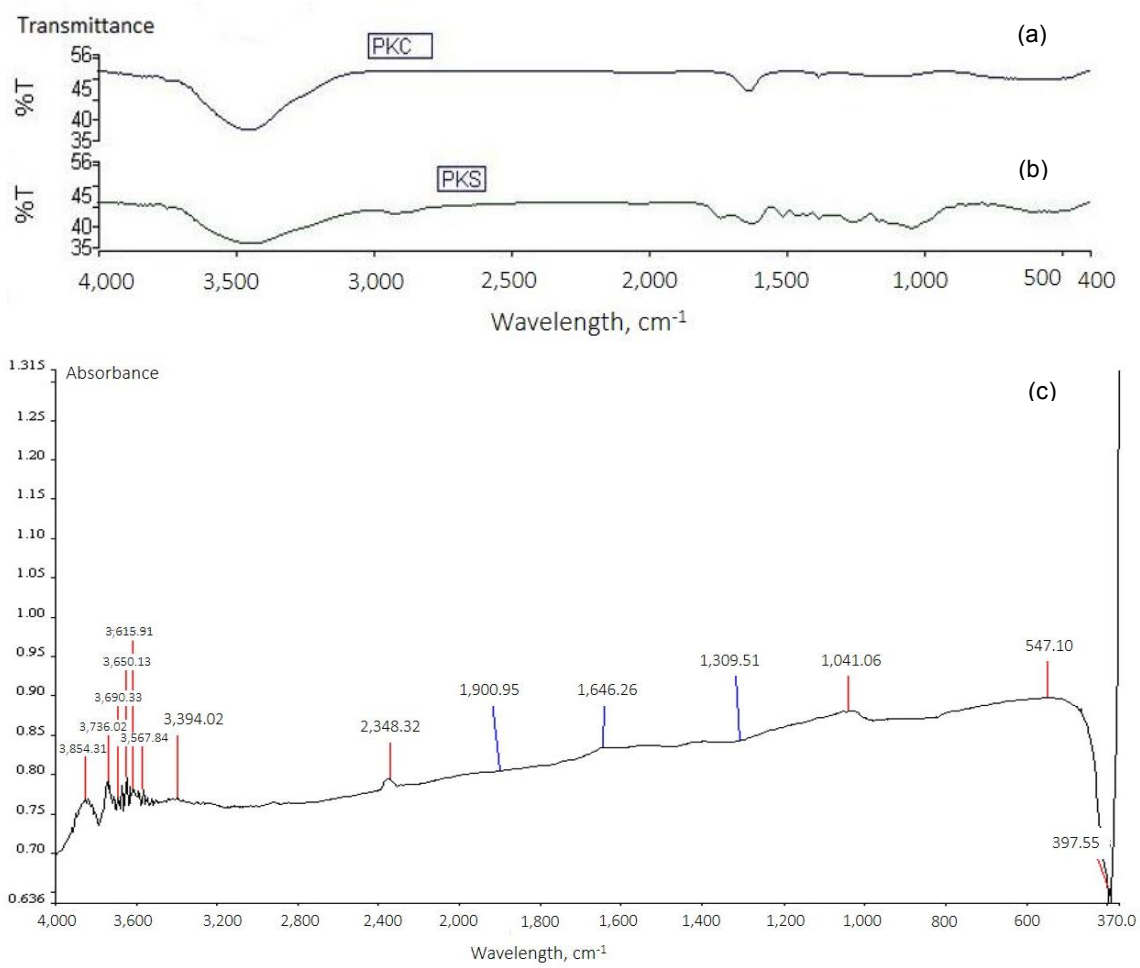


Figure 2: FTIR analysis on (a) PKS, (b) PKC, (c) PKAC-$FeCl_3$

3.2 Single gas adsorption in breakthrough study

3.2.1 Breakthrough time of single gas adsorption

This research studied detail about the breakthrough time and saturation time behaviour for SO_2 and O_2 adsorption on palm shell activated carbon. The results obtained from experiment are compared to the results obtained from calculation using Yoon equation. Based on the results, SO_2 adsorption produced has longer breakthrough time compared to the adsorption of O_2. PKAC-$FeCl_3$ recorded 23 s breakthrough time of SO_2 adsorption for 3.6 g weight sample. The longer the breakthrough time for the adsorption of the poisoning gas means that the better the adsorbent's performance. PKAC-$FeCl_3$ produced good performance in SO_2 adsorption might be due to the strong bond between adsorbent and SO_2 in term of surface interaction. The adsorption of SO_2 might be due to physisorption (interaction SO_2-Fe^{3+}) in adsorbent (Sirisha et al., 2015). The performance also might be depending on the properties of the gas. Oxygen adsorption testing was used as reference for the human breathing. PKAC-$FeCl_3$ produced shorter breakthrough time in O_2 adsorption and this result was good for the air filtration safety device. Table 2 shows the comparison of breakthrough time results obtained from experimental and calculation. Based on the results obtained, the Yoon equation can be used for determining the breakthrough and saturation time.

Table 2: Breakthrough time for 3.6 g of activated carbon (experiment and calculation)

Sample	Breakthrough time(s) (exp.)	Breakthrough time(s) (calc.)
SO_2	23	23.2
O_2	7.5	7.3

3.2.2 Saturation time of single gas adsorption

The saturation time of SO_2 and O_2 adsorption on PKAC-$FeCl_3$ are shown in Figure 3 and Table 3. The saturation time were obtained using Yoon equation. For the experimental results, only the breakthrough times were determined because it cannot achieve the saturation level due to limited gas and the gas used only at 10 ppm. Saturation time of SO_2 and O_2 on PKAC-$FeCl_3$ were recorded at 7,680 s and 2,400 s.

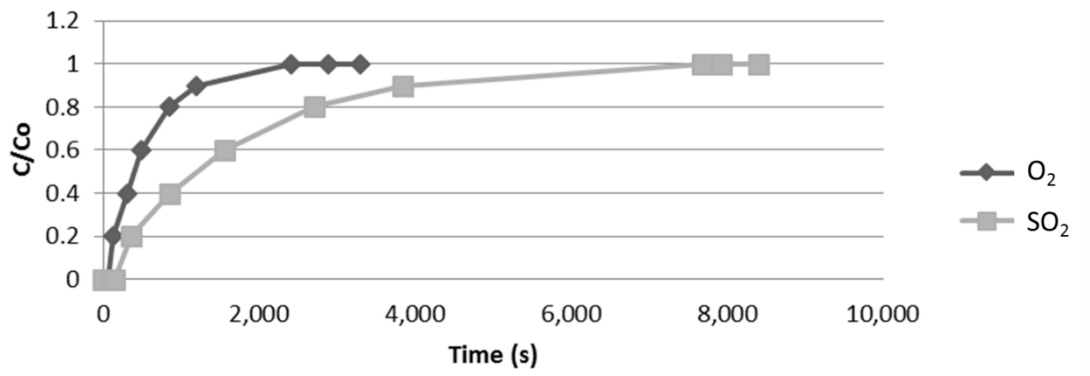


Figure 3: Saturation time for SO_2 and O_2 adsorption

Table 3: Saturation time for 3.6 g of activated carbon (calculation)

Gas	Saturation time (s)
SO_2	7,680
O_2	2,400

4. Conclusions

The breakthrough time of SO_2 and O_2 single gas adsorption on the PKAC-$FECl_3$ were obtained at 23 and 7.5 s. The PKAC-$FECl_3$ sorbent recorded longer breakthrough time of 23 s for SO_2 adsorption at 100 mL/min inlet flow rate. The adsorption breakthrough experimental data was compared with the data obtained from Yoon equation. The breakthrough study showed that activated carbon derived from palm shell is a potential material to be used as respiratory media in the purification and filtration system.

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References

Adinata D., Daud W.M.A.W., Aroua M.K., 2007, Preparation and characterization of activated carbon from palm shell by chemical activation with K_2CO_3, Bioresource Technology 98, 145-149.

Aksu Z., Gönen F., 2004, Biosorption of phenol by immobilized activated sludge in a continuous packed bed: prediction of breakthrough curves, Process Biochemistry 39, 599–613.

Auta M., Hameed B.H., 2013, Coalesced chitosan activated carbon composite for batch and fixed-bed adsorption of cationic and anionic dyes, Colloids and Surfaces B: Biointerfaces 105, 199-206.

Chingombe P., Saha B., Wakeman R.J., 2005, Surface modification and characterisation of a coal-based activated carbon, Carbon 43, 3132–3143.

Choo H.S., Lau L.C., Mohamed A.R., Lee K.T., 2013, Hydrogen sulfide adsorption by alkaline impregnated coconut shell activated carbon, Journal of Engineering Science and Technology 8, 741 – 753.

Din A.T.M., Hameed B.H., Ahmad A.L., 2009, Batch adsorption of phenol onto physiochemical-activated coconut shell, Journal of Hazardous Materials 161, 1522–1529.

Foo K.Y., Hameed B.H., 2009, Recent developments in the preparation and regeneration of activated carbons by microwaves, Advances in Colloid and Interface Science 149, 19–27.

Foo K.Y., Hameed B.H., 2011, Preparation of oil palm (Elaeis) empty fruit bunch activated carbon by microwave-assisted KOH activation for the adsorption of methylene blue, Desalination 275, 302–305.

Hamza U.D., Nasri N.S., Mohammed J., Zain H.M., 2015, Thermal regeneration of CO_2 spent palm shell-polyetheretherketone activated carbon sorbents, International Journal of Chemical, Nuclear, Materials and Metallurgical Engineering 9, 492-495.

Liu Q.S., Zheng T., Li N., Wang P., Abulikemu G., 2010, Modification of bamboo based activated carbon using microwave radiation and its effects on the adsorption of methylene blue, Applied Surface Science 256, 3309–3315.

Mohammed J., Nasri N.S., Zaini M.A. A., Hamza U.D., Zain H.M., Ani F.N., 2015, Optimization of microwave irradiated - coconut shell activated carbon using response surface methodology for adsorption of benzene and toluene, Desalination and Water Treatment 57 (17), 7881-7897.

Mubarak N.M., Kundu A., Sahu J.N., Abdullah E.C., Jayakumar N.S., 2014, Synthesis of palm oil empty fruit bunch magnetic pyrolytic char impregnating with $FeCl_3$ by microwave heating technique, Biomass and Bioenergy 61, 265-275.

Nasri N.S., Hamza U.D., Ismail S.N., Ahmed M.M., Mohsin R., 2014, Assessment of porous carbons derived from sustainable palm solid waste for carbon dioxide capture, Journal of Cleaner Production 71, 148-157.

Rugayah A.F., Astimar A.A., Norzita N., 2014, Preparation and characterisation of activated carbon from palm kernel shell by physical activation with steam, Journal of Oil Palm Research 26, 251-264.

SEA (Safety Equipment Australia), 1997, The practical use of some existing models for estimating service life of gas filter, Safety Equipment Australia Pty Ltd, Sydney, Australia.

Sirisha D., Smita A., Gandhi N., Hasheena M., 2015, Adsorptive removal of aqueous SO_2 by using Orange Peel Powder, Indian Journal of Science 12, 39-51.

Sumathi S., Bhatia S., Lee K.T., Mohamed A.R., 2010, Adsorption isotherm models and properties of SO_2 and NO removal by palm shell activated carbon supported with cerium (Ce/PSAC), Chemical Engineering Journal 162, 194–200.

Wade L.G., 2010, Organic Chemistry, Pearson Education, New Jersey, United States, 1243-1262.

Zhang P., Wanko H., Ulrich J., 2007, Adsorption of SO_2 on activated carbon for low gas concentrations, Chemical Engineering Technology 30, 635–641.