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Kinetic, Thermodynamic and Regeneration Studies for CO_2 Adsorption onto Activated Carbon

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Abstract

Removal of CO_2 from flue gases has become an effective way to mitigate the Green House Gas effects and Pressure swing adsorption (PSA) is a potential technique for removing CO_2 from a flue gas streams. Low cost and abundantly available, activated carbon (coconut fibre) is a suitable candidate sorbents in the PSA process for CO_2 adsorption. Adsorption tests have been carried out in a fixed-bed column, at different temperatures starting from 25 ˚C to 60 ˚C and at a pressure up to 1 bar in order to investigate both kinetic and thermodynamic parameters. Moreover, regeneration studies have been conducted in order to verify the possibility of activated carbon reutilization, to determine its CO_2 adsorption capacity within consecutive cycles of adsorption–desorption. It was established that the activated carbon has a good CO_2 adsorption capacity, likely related to its surface area and composition, as well as to the intrinsic nature of the solid. CO_2 adsorption rate increases with increase in pressure while increase in temperature reduces the adsorption capacity. Experimental results confirmed that CO_2 adsorption is a reversible process and that desorption temperature is the main controlling parameter. The experimental data was fitted with Langmuir model and fit well with the experimental data of 2.828 $mol_{CO_2} kg_{cat}^{-1}$. The thermodynamics parameter shows that the CO_2 adsorption process is exothermic in nature.

Keywords: Pressure swing adsorption, Adsorption isotherm, Activated carbon, thermodynamics parameter.

1. Introductions

The increase in worldwide CO_2 emissions, mainly deriving from fossil fuel combustion is commonly believed to be among the main contributors for global warming. Currently, 85% of total world demanded energy is supplied by thermal power plants fed by fossil fuels, including coal, oil and gas. They account for about 40% of total CO_2 emissions (Metz et al., 2005). Nowadays, many options to reduce CO_2 emissions by retrofitting at their point sources are available. In particular, post-combustion technologies such as absorption, adsorption, gas separation membrane, cryogenic separation, etc. seem to have the greatest near-term potential for CCS applications, because they can be retrofitted to existing units. Moreover, they have higher thermal efficiency than pre-combustion technologies, even if CO_2 concentration in flue-gas is typically lower than 15% (Xang et al., 2008). The low CO_2 concentration determines a low thermodynamic driving force available for CO_2 capture. Hence, to achieve a high level of CO_2 removal, large gas volumes have to be treated with high equipment and operational costs. These issues drive to the development of cost effective CO_2 advanced capture processes.

In this scenario, adsorption seems to be a very promising technology, widely used for gas treatment due to its good removal efficiency, great versatility and, if coupled with an effective regeneration process, for the absence of by-products. Many different sorbents can be used on purpose; activated carbons are generally less costly than other materials (e.g., zeolites, mesoporous silicas, metal organic frameworks, etc.) (Pellerano et al., 2009), and in some cases they also show comparable adsorption capacity . Generally, activated carbon is easily generable due to a low heat of adsorption. Regeneration can be carried out either by increasing the temperature (Temperature Swing Adsorption) or by decreasing the pressure, at atmospheric value (Pressure Swing Adsorption) or under vacuum (Vacuum Swing Adsorption,) (Tlili et al., 2009). The high potentiality of activated carbon for CO_2 capture relies in their complex structure characterized by high surface area, tunable porosity.

This paper presents CO_2 adsorption on a low cost and abundantly available activated carbon (coconut fibre) at a temperature starting from 25 ˚C to 60 ˚C and at a pressure up to 1 bar. Kinetic and thermodynamic aspects of CO_2 adsorption were investigated in order to define the real potentiality of the activated carbon for post-combustion CO_2 capture. Finally, regeneration studies were conducted in order to verify the possibility of a carbon reutilization, to determine its CO_2 adsorption capacity within five consecutive cycles of adsorption–desorption.

2. Materials

The activated carbon (coconut fibre) used was obtained from a local area. It was pilled and the fibrous part was collected and was broken into small pieces. The coconut fibre was washed with water, dried in the sun for 10 hrs and transfer to the furnace. The coconut pieces were burnt distinctively in the furnace for an hour at a temperature of 350 °C. The charcoal produced was withdrawn from the furnace and sieved which gives a mean particle diameter of 192 µm. The material characterization was done for

proximate and ultimate analysis and details of the physical and chemical properties are given below in Table 1.

3. Experimental Set-up and Procedures

The experimental set-up for the adsorption test consists of a CO_2 cylinder and Gas Compressor interconnected through a pipe to the system as shown in Fig. 1. The Gas Compressor could provide sufficient pressure up to 10 kg/cm^2 with a discharge capacity of 84 LPM. The gas mixing chamber was made up of a GI pipe of 20 mm diameter and 80 mm in length to achieve the require mixture of air and CO_2 (13.8 vol. %) at a constant rate. Ceramic wool was wrapped around the reactor above the heater coil and thermocouples were inserted in the bed to measure the bed temperatures.

A Glass Tube Rotameter of the range 0-35 LPM was used to control the mass flow rate and measure the mass flow rate of the incoming gas. The reactor was made up of GI pipe with 30 mm diameter with 1.5 mm wall thickness and 200 mm in height. A pressure monitoring system was attached to know the incoming pressure and experiments were carried at varying pressure to see the effect of pressure in the adsorption process at a constant temperature. A number of needle valves were attached in the system to control the system operation at the require rate. Flue Gas Analyzer (KM9106) was used to measure the inlet sample gas and the outlet gas properties. The apparatus was tested for leak absence and for accuracy through calibrations with an empty tank. Table 2 give details of the operating parameters.

Table 1: Properties of activated carbon.

BET surface area (m2/g)			214
Pore volume (cc/g)			0.0683
Bulk density (kg/m3)			350
Particles diameter (µm)			192
Ultimate Analysis (wt %)			
C	O	Cl	K
41.28	36.00	6.01	33.71
Proximate Analysis (wt %)			
Ash	Moisture	Fixed Carbon	Volatile
4.8	10.63	14.49	70.08

Table 2: Experimental conditions.

Bed weight	20 g
Reactor length	200 mm
Reactor diameter	30 mm
Influent CO2 concentration	13.8 vol.%
Inlet flow rate	15 LPM
Bed porosity	0.5
Superficial velocity	0.13 m/s
Adsorption temperature	25-60 °C
Adsorption total pressure	1 bar

The process employed a single-bed pressure swing adsorption unit. For the adsorption process, first the air was allowed to flow through the reactor and then followed by carbon dioxide. To maintain equal flow rate and pressure of both the flows, the gas mixture was allowed to pass through the mixing chamber. The flow of air was then stopped and allowed only the pure CO_2 to flow through the reactor for measurement of the mass of CO_2 adsorbed per the mass of the adsorbent. To know the effective adsorbed mass on the adsorbent materials $Q_{eff,}$ two quantities were defined: Q_t

that is the mass containing the reactor including the adsorbents and Q_d which is the mass of the empty reactor or dead volume. The Q_{eff} was then calculated with the equation as follows: $Q_{eff}=Q_t-Q_d$.

4. Results and Discussions

4.1 Adsorption isotherms

Adsorption isotherm of CO_2 with activated carbon is shown in Fig. 2 and shows that the adsorption of CO_2 was taking place moderately till 1 bar. The adsorption capacity was found out to be 2.0 to 2.828 $mol_{CO_2} kg_{AC}^{-1}$ of the sorbent at a pressure range between 0.4 bar to 1 bar. It was reported by Sircar et al., 2006 that the adsorption capacities of activated carbon increases moderately till 30 bar and becomes steady after 30-35 bar. It can also be concluded that by increasing the pressure there is a corresponding increase in CO_2 adsorption while the adsorption decreases with increase in temperature. This is due to the fact that increase in the temperature excited the internal energy of the adsorbent which tends to release the CO_2 molecules present on the adsorbent.

Material aging or regeneration studies was conducted and it was interesting to note that all the isotherms were extremely reproducible, which indicates the excellent reversibility of adsorption. The adsorption isotherms of CO_2 at different temperatures on activated carbon samples were fitted to standard Langmuir isotherm models by linear regression. The Langmuir isotherm equation can be represented by equation 1.0 (Guo et al., 2006):

$$q = \frac{q_m K P_{CO_2}}{1 + K P_{CO_2}} \tag{1.0}$$

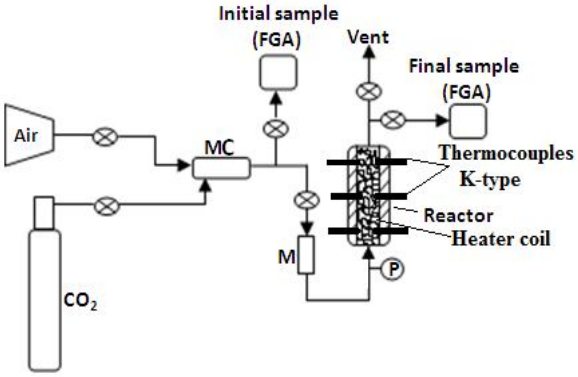

Fig. 1: Schematic of the experimental set-up. MC: Mixing chamber; M: Mass flow meter; P: Pressure gauge; FGA: Flue Gas Analyzer.

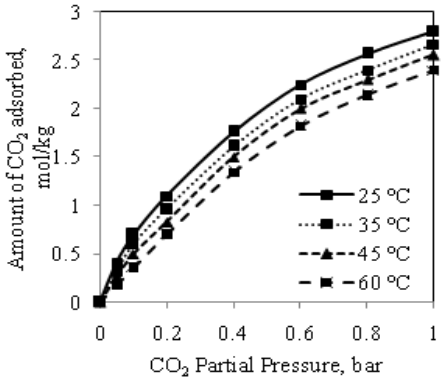

Fig. 2: CO2 adsorption isotherm on Activated Carbon.

where q is the amount of CO_2 adsorbed at the CO_2 partial pressure P and q_m is the amount of CO_2 adsorbed with monolayer coverage. The values of q_m and Langmuir constant K, calculated from the CO_2 adsorption isotherms, are listed in Table 3. The

monolayer CO_2 coverage at the different temperatures 25 °C, 35 °C, 45 °C and 60 °C were well fitted for the adsorbents. Results show that the maximum loading, q_m varies almost linearly with the temperatures.

4.2 Effect of temperatures and adsorption thermodynamics

The thermodynamic parameters were calculated from the Langmuir isotherms by using the Vant'Hoff's equation as given in equations 2.0 to 4.0. The detail parameters for CO_2 adsorption on activated carbon are given in Table 3. The temperature effect on the adsorption of CO_2 were studied at 25°C, 35°C, 45 °C and 60 °C. From adsorption isotherm curve in Fig. 2, it can be seen that by increasing the bed temperature there is a decrease in CO_2 adsorption capacity which is due to the exothermic nature of the adsorption process. The optimum temperature for CO_2 adsorption on the adsorbent was found to be 25 °C within the temperature range studied. The thermodynamic parameters can be calculated from the Langmuir isotherms by using the Vant'Hoff's equation as follows (Alzaydien and Manasreh, 2009):

$$\Delta G^{\circ} = -RT \ln K_l \tag{2.0}$$

$$\Delta H^{\circ} = R \frac{T_1 T_2}{T_2 - T_1} \ln \frac{K_2}{K_1} \tag{3.0}$$

$$\Delta S^{\circ} = \frac{\Delta H^{\circ} - \Delta G^{\circ}}{T} \tag{4.0}$$

where ΔG° is change in the Gibb`s free energy, ΔH° is change in the enthalpy and ΔS° is change in the entropy. The enthalpy change, ΔH° and the entropy change, ΔS° are -14.98 kJ/mol and 24.379 J/mol.K respectively. The negatives values of ΔG° confirm the feasibility of the process and the spontaneous nature of the adsorption process. The negative values in ΔH° indicated that the adsorption reaction is exothermic for both the adsorbent used while the positive value of ΔS° reflects the affinity of the adsorbents with CO_2.

Table 3: Langmuir and thermodynamic parameters.

Material	**Temp (°C)**	**Langmuir constants**		**R2**	**ΔG° (kJ/mol)**	**ΔH° (kJ/mol)**	**ΔS° (J/mol.K)**
		qm (mol/kg)	K				
Activated carbon	25	2.828	21.956	0.991	-7.653	-14.98	24.379
	35	2.711	19.119	0.993	-7.556		
	45	2.591	15.502	0.998	-7.247		
	60	2.494	11.759	0.997	-6.824		

5. Conclusions

In this study, a single-bed pressure swing adsorption process was employed to determine the adsorption capacity of activated carbon. The results showed that activated carbon (coconut fibre) have relatively considerable potential for CO_2

adsorption. The experimental data's were fitted with Langmuir model and found to fit well with the experimental data. The result also shows that there can be a complete regeneration for Activated Carbon. The thermodynamics parameter shows that the CO_2 adsorption process is exothermic in nature.

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