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Kinetic Studies on Carbon Dioxide Capture using Activated Carbon

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Global warming and global climatic changes resulted from anthropogenic carbon dioxide (CO_2) emissions has become the main issue recently. Since the beginning of industrial revolution, the concentration of CO_2 has increased more than 30 % in the atmosphere, and resulted in various catastrophic occurrences. This study focused on the influence of temperature at 25, 50, and 100 °C towards the CO_2 adsorption capacity. Maximum CO_2 sorption capacity on the synthesized activated carbon is found to be 80 mg CO_2 per gram adsorbent. Experimental data is modelled through Lagergren first-order, pseudo-second-order, and intra-particle diffusion model. From the correlation coefficient, it is found that the pseudo-second-order model is well-fitted with the experimental data. In addition, the activation energy is found to be less than 42 kJ/mol, and it is proved that the physical adsorption occurs.

1. Introduction

Rising of carbon dioxide (CO_2) emission is mainly caused by the utilization of non-renewable and carbon emitting fuels such as coal, petroleum and natural gas. Accelerated consumption of these resources undeniably causes lots of dreadful impacts towards the ecology, specifically the major long-term climatic changes i.e. global warming. Global warming is largely contributed by CO_2, followed by methane, ozone and chlorofluorocarbon (Purba and Taharuddin, 2010). These greenhouse gases block the Sun's energy from escaping to the space, and thus keep the atmosphere warm. Yet, rising level of greenhouse gases in the atmosphere causes the blanket to be thicker and accordingly, increases the surface temperature and eventually leads to global warming. By 2035, CO_2 concentration is estimated to reach about 550 ppm and results in temperature rise of 2 °C, which will threaten 15 to 40 species with extinction (Hileman, 2006). Considering the continuous usage of fossil fuels in electricity and power generation, the idea of carbon capture and storage (CCS) is proposed to abate the greenhouse gases emission, particularly CO_2. At present, chemical absorption using the amine-based solvent is the most matured technology that is applicable in industry. However, Murshid et al. (2011) reported that amine consumption has few limitations, such as low CO_2 absorption capacity, high energy penalty during absorbent regeneration, amine degradation, and potential of corrosion. Hence, solid adsorption is proposed to overcome the existing technology's limitations. Carbon materials such as activated carbons is attractive as CO_2 adsorbent due to its wide availability, high thermal stability, low cost, and low sensitivity to moisture (Plaza et al., 2012). The objective of the present work is to evaluate the kinetic properties of purified CO_2 adsorption onto the agro-waste activated carbon, with respect to various adsorption temperatures. Kinetic models such as pseudo-first-order model, pseudo-second-order model, and intra-particle diffusion model are tested in this study. These models' goodness is evaluated by the magnitude of coefficient of determination (R^2), and the closer the value to unity, the better the model will be, as it implies that the model predicts closer data value to the experimental data.

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2. Experimental

2.1 Preparation of activated carbon

The agro-waste based activated carbon were dried and prepared as described by Rashidi et al. (2012). The activation process under the CO_2 flow (99.8 % purity) was carried out by following the Taguchi experimental design of L_{25} orthogonal array. Taguchi method is useful in planning experimental work, as it reduces number of total experiments needed, and thus, minimizes time and cost while performing the experiments.In this study, six parameters with five levels each were studied, as shown in Table 1.

Table 1: Design factors and levels for activation process

Process parameter	Unit	Level 1	Level 2	Level 3	Level 4	Level 5
Precursors	-	Palm fiber	Palm shell	Rice husk	Coconut shell	Coconut fiber
Particle size	μm	250	355	500	710	1000
Heating rate	^oC/min	5	10	15	20	25
CO_2 flow rate	cm^3/min	100	150	200	250	300
Temperature	^oC	500	600	700	800	900
Holding time	min	15	30	45	60	90

2.2 Isothermal CO_2 adsorption/desorption

CO_2 adsorption/desorption studies were performed by using a thermal gravimetric analyzer (EXSTAR TG/DTA 6300). The process involved placing samples (5-10 mg) into an alumina pan and the operating temperature was adjusted to adsorption temperature of 25, 50 and100 ^oC under the purified CO_2 (99.98 % purity), at flow rate of 50 cm^3/min. Prior to the adsorption process, the sample materials were activated at 120 ^oC under a vacuum condition overnight, to ensure that an excess moisture had been entirely removed. Once the equilibrium state achieved, desorption process was carried out by switching the gas to pure nitrogen (50 cm^3/min) at the same temperature. The exposure time of adsorption and desorption time was 2 h each. For comparison purposes, the commercial activated carbon of size 250 μm was used. The amount of CO_2 molecules adsorbed onto the synthesized activated carbon (mg/g) was calculated based on Eq. (1), where w_t and w_o represents mass of adsorbent at time t and original mass of adsorbent, respectively.

$$CO_2 \, Adsorption = \frac{w_t(mg) - w_o(mg)}{w_o(g)} \tag{1}$$

3. Results and discussions

3.1 General characteristics of activated carbon

A series of activated carbon were developed according to the orthogonal array determined. In our study, commercial and optimized activated carbons were tested for the kinetic analysis. The optimized activated carbon referred to the coconut shell of size 250 μm, and at operating condition of 900 ^oC with 20 ^oC/min heating rate, and at 45 min holding time under the 150 mL CO_2 flow, which had the utmost CO_2 adsorption capacity, around 79 mg/g. In contrast, the commercial activated carbon had an adsorption capacity of 81 mg/g. The chemical compositions of the raw precursors, optimized and commercial activated carbon were summarized in Table 2.

Table 2: Chemical compositions of the precursors (coconut shell), optimized and commercial activated carbon

Parameters	Raw coconut shells	Optimized activated carbon	Commercial activated carbon
Elemental analysis (wt %):			
Carbon	50.08	88.18	72.38
Hydrogen	6.08	1.32	2.10
Nitrogen	0.05	0.40	0.20
Sulphur	0.62	0.25	0.27
Oxygen	43.25	9.87	25.05
Moisture content (wt %)	1.91	1.43	2.21

According to Table 2, both raw material and activated carbons that have moisture content less than the recommended value (less than 3 %) is very significant and ideal for storage purposes. The significance of having lower moisture content in solid sorbent is due to the potential of fungi growth and multiplication, which will result in carbon degradation and pore blockage (Hapazari et al., 2011). Upon activation process, the heat treatment of the precursors causes reduction of moisture and volatiles matters, while enhancing the carbon content. In addition, surface morphology of the carbonaceous materials were studied, and it is evidently shown that the precursor has a rough surface, porous-less and without any cracks or cavities as shown in Figure 1(a). On the other hand, the produced activated carbon has some cavities and hollows (as shown in Figure 1(b)), which was attributed by the devolatilization of inorganic materials that were initially attached to the carbon wall.

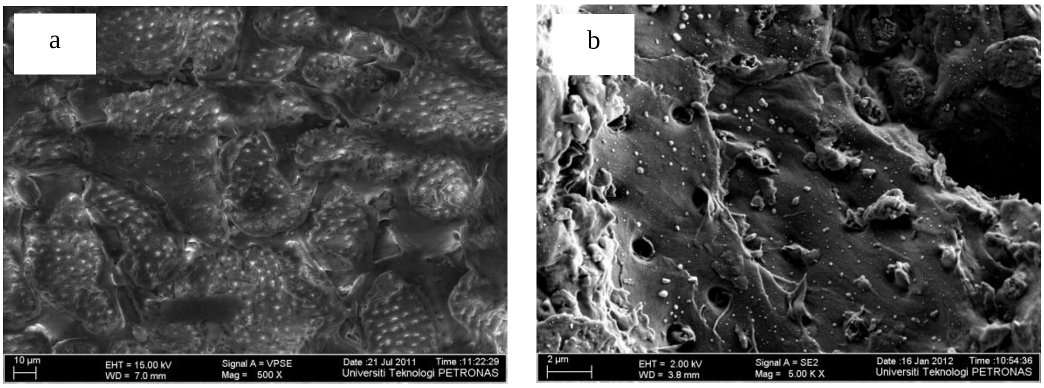

Figure 1: FESEM image of (a) raw coconut shell, and (b) coconut-shell activated carbon.

3.2 CO_2 adsorption/desorption

Figure 2 illustrates the adsorption profiles at different reaction temperatures of both the commercial and optimized activated carbon. Based on Figure 2, it shows that the rate of CO_2 adsorption gradually decreased with contact time, until an equilibrium condition was achieved. The CO_2 adsorption was most intensive during the first 40 min, and thereafter remains unchanged until saturation was attained. The rapid adsorption rate could be attributed to the sorbent surface area which is accountable for interaction with the CO_2 molecules. Over time, the adsorption rate is observed to be decreased due to reduction of active sites that may slow down the adsorption process from taking place. In addition, Li et al. (2008) suggest that the rapid adsorption at the beginning of the process is due to external surface of the adsorbent, and is followed by slower internal diffusion process.

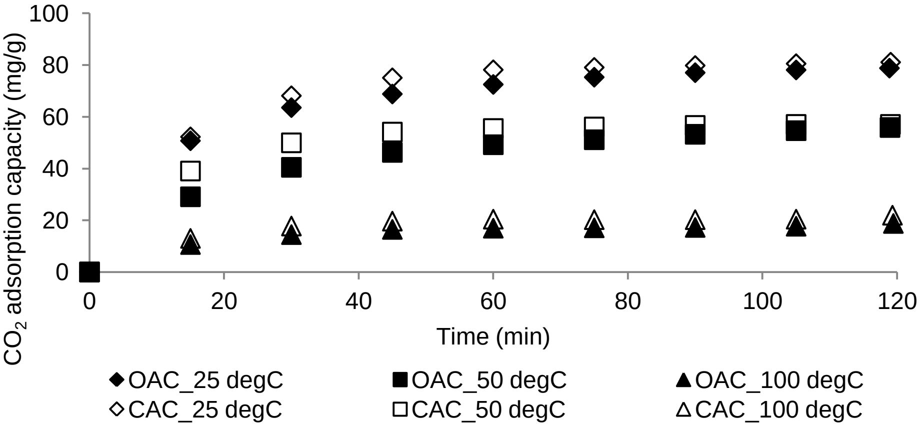

Figure 2: Adsorption profiles of commercial and optimized activated carbon at 25, 50 and 100 °C (OAC = Optimized activated carbon; CAC = Commercial activated carbon)

In post-combustion processes, the flue gas temperature is typically within the range of 50 to 120 °C (Kaithwas et al., 2012). Thus, an adsorption study was conducted at 50 and 100 °C to investigate the CO_2 adsorptive properties at an elevated temperature. Figure 2 and Table 3 show that the CO_2 adsorption capacity of both solid adsorbents decreases with temperature, and it implies the existence of physical adsorption (physisorption) between the CO_2 molecules and carbonaceous adsorbent. Maroto-Valer et al. (2005) reported that physisorption process involves high surface adsorption energy and molecule diffusion at elevated temperatures, which results in instability of the adsorbed gas on the surface of activated carbon and consequently, desorption process will occur. In our study, almost complete CO_2 regeneration was observed during the desorption process (shown in Table 3), and it indicates the presence of weaker interaction bonding between the adsorbate and adsorbent. It is supported by Shafeeyan et al. (2011) who reported that the chemisorption between the CO_2 molecules and modified activated carbon results in the lowest desorption capacity (91.9 wt%), despite of its highest CO_2 adsorption capacity. This is due to strong affinity of CO_2 and solid adsorbent that hinder the regeneration/desorption process. In contrast, weaker bonding between the CO_2 molecules and activated carbon lead to the highest desorption capacity, around 99.4 wt%. In practical, adsorption and desorption capacity must be balanced to achieve the techno-economic feasibility.

Table 3: CO_2 adsorption-desorption behaviour on the activated carbon

Adsorbent	Temperature (^oC)	CO_2 uptake (wt%)	Desorption (wt%)
Optimized activated carbon	25	7.88	98.70
	50	5.58	99.13
	100	1.89	100.00
Commercial activated carbon	25	8.11	100.00
	50	5.70	100.00
	100	2.19	100.00

3.3 Kinetic analysis

The kinetic analysis establishes an adsorption uptake rate and determines the residence time for the adsorption process to be completed. It is also a baseline on determining the adsorption dynamics and its performance in real application, such as in fixed-bed or in flow-through systems. Thus, Lagergren pseudo-first-order model and pseudo-second-order model was performed in this work. The conformity of the experimental work and kinetic model was analyzed by the R^2 values. The linearized Lagergren pseudo-first-order is generally expressed by Eq. (2) (Ho and McKay, 1998).

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303} t \qquad (2)$$

Based on Eq. (2), q_e and q_t are the adsorption capacity (mg/g) at equilibrium and at time t, respectively and k_1 is the rate constant of pseudo-first-order model (1/min). The straight line plot of log (q_e-q_t) versus time (t) was made at various adsorption temperatures for both of the activated carbons, and the parameters were tabulated in Table 4. It was observed that the pseudo-first-order kinetic model for both activated carbons did not fit well with the experimental data, with R^2 value was found to be within the range of 0.73 to 0.98.

Table 4: Kinetic parameters of the activated carbons (OAC = Optimized activated carbon; CAC = Commercial activated carbon)

Kinetic model	Parameter	Temperature (^oC) 25		50		100	
		OAC	CAC	OAC	CAC	OAC	CAC
Pseudo-first-order	k_1 (1/ min)	0.039	0.042	0.032	0.049	0.020	0.018
	q_e (mg/g)	55.463	45.709	43.471	32.300	7.903	7.147
	R^2	0.984	0.987	0.986	0.990	0.887	0.728
Pseudo-second-order	q_e (mg/g)	86.207	86.957	63.694	60.606	20.120	22.989
	k_2 (g/mg·min)	1.076E-3	1.370E-3	8.844E-4	2.482E-3	4.002E-3	4.450E-3
	h (mg/g·min)	7.994	10.363	3.588	9.116	1.620	2.352
	R^2	1.000	0.999	1.000	0.999	0.996	0.995

In addition, pseudo-second-order model and initial rate of adsorption, *h* (mg/g·min) is expressed by Eq. (3) and Eq. (4) (Ho and McKay, 1998).

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^{\ 2}} + \frac{1}{q_e} t \qquad (3)$$

$$h = k_2 q_e^{\ 2} \qquad (4)$$

For the Lagergren pseudo-first-order model, q_e and q_t represents the amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium and at any time (t). If the pseudo-second-order kinetic model is applicable in the adsorption process, plot of t/q_t against time will result in a straight line with $1/h$ and $1/q_e$ is the y-intercept and slope, respectively. Comparing the value of regression coefficient as stated in Table 4, pseudo-second-order model gives better fit than the Lagergren first-order model. In addition, the initial adsorption rate (h) was observed to decrease with respect to temperature. It is explained by higher kinetic energy of the CO_2 adsorbate at elevated temperatures, which resulted in its increasing tendency to escape from the surface of activated carbon.

In contrast to Lagergren pseudo-first-order and pseudo-second-order model, intra-particle diffusion model provides an insight of the mechanism in adsorption process. Adsorption consists of few steps involve the transport of adsorbate from the bulk phase to the surface of solid sorbent, and is followed by the molecules diffusion into the interior of the pores. Intra-particle diffusion normally is described as a slow process and is a rate-limiting step in many of adsorption processes, and it can be expressed by Eq. (5) below (Ho et al., 2000).

$$q_t = k_{id} t^{1/2} + C_i \qquad (5)$$

According to Eq. (5), q_t represents the amount of CO_2 adsorbed at any particular time (mg/g), k_{id} is the intra-particle rate constant (mg/min·$t^{1/2}$), and t is the contact time (min$^{1/2}$). Plot of q_t against the square root of t is illustrated in Figure 3. Theoretically, if the adsorption process obeys the intra-particle diffusion model, a straight linear plot that passes through the origin is expected. However, Figure 3 shows variation of gradient with respect to time and it indicates that the intra-particle diffusion is not the sole rate-limiting step in this adsorption process. Based on Figure 3, the first steeper region (4-7 min$^{1/2}$) could be due to surface sorption, whilst the second region (7-11 min$^{1/2)}$ may be attributed by the intra-particle diffusion rate-controlled.

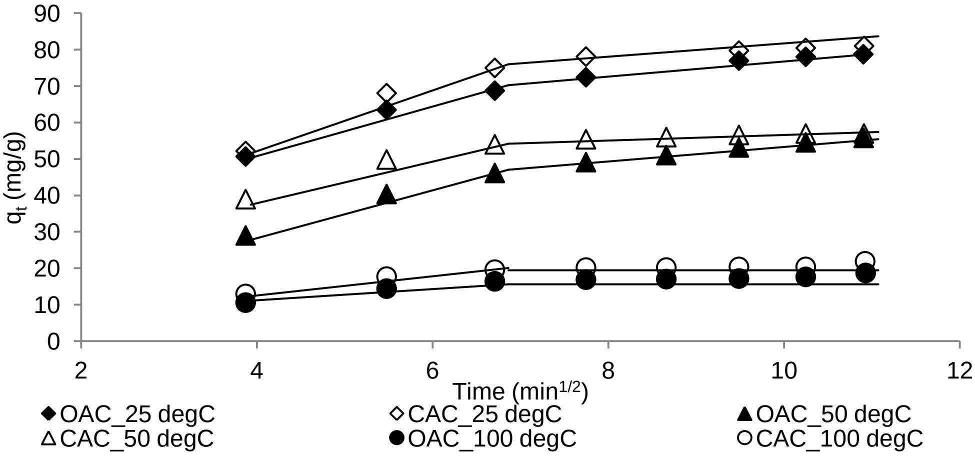

Figure 3: Intra-particle diffusion study (OAC = Optimized activated carbon; CAC = Commercial activated carbon)

The magnitude of the activation energy (E_a) is important in any of adsorption process, as it provides insight information on the mechanism of the adsorption process. Since the physical adsorption involves weak bonding between the adsorbate and adsorbent, the value of activation energy is usually around 5 to 40 kJ/mol, whilst the chemisorption process has activation energy of 40 to 800 kJ/mol (Özcan et al., 2006). To calculate the activation energy of the adsorption process, the Arrhenius equation that is shown in Eq, (6) is applied (Özcan et al., 2006).

$$\ln k = \frac{-E_a}{RT} + \ln k_o \tag{6}$$

In Eq. (6), k is the rate constant of pseudo-second-order kinetic model (g/mg·min), E_a is the adsorption activation energy (J/mol), R is the gas constant (8.314 J/mol·K), T is the adsorption temperature in Kelvin, and k_o is the temperature independent factor (g/mg·min). Upon calculation, it shows that the activation energy for optimized and commercial activated carbon is 17.51 and 14.27 kJ/mol, respectively. In addition, lower activation energy found in this work implies that the CO_2 adsorption onto the activated carbons is a diffusion-controlled process, rather than the chemically-controlled.

4. Conclusions

This study shows that the low-cost activated carbon can be produced from the coconut by-products. The utilization of the coconut waste is promising as it consists of mainly carbon and low in inorganic content, aside from the minimization of the waste problems. The CO_2 activation is found to develop porosity of the activated carbon, which assists the adsorption process. Comparability in the CO_2 adsorptions capacity and complete desorption indicates the practicality of the synthesized activated carbon to be used in industrial applications. Further, the equilibrium and kinetic of CO_2 adsorption onto the activated carbon has been studied. The magnitude of activation energy which is lesser than 40 kJ/mol indicates an occurrence of the physisorption mechanism. Besides, the kinetic analysis demonstrates that the CO_2 adsorption onto the activated carbon obeys the pseudo-second-order model, due to its closer R^2 value to unity.

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