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CO_2 Adsorption Equilibria on a Hybrid Palm Shell-PEEK Porous Carbons

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CO_2 emission is attributed to be the major contributing factor for global warming. In this work, hybrid porous carbons were prepared by K_2CO_3 microwave assisted activation of palm shell with polyetheretherketone (PEEK). The Porous carbons (M4P2 and M5P2) were investigated as potential sorbents for CO_2 capture at various temperatures. The ideal CO_2 adsorption capacities of porous carbons were determined using volumetric method at temperatures of 303.15 and 243.15, 378.15 and 443.15 K and pressures (1-4 bar). CO_2 uptake of 2.97 and 2.55 mmol CO_2 adsorbed/g adsorbent was achieved by M4P2 and M5P2 sorbents at 30 °C and 1 bar. The experimental data of the CO_2 adsorption on the porous carbons were correlated by the Freundlich, Langmuir, Toths and Sips isotherm models. Sips adsorption isotherm model fits the data better with higher correlation coefficient and low root mean square deviation (RSMD) at all temperatures. CO_2 adsorption was faster initially and then subsequently decreased with time. The findings revealed the potential of palm shell-PEEK as sorbents for CO_2 adsorption applications.

1. Introduction

Release of carbon dioxide primarily due to combustion of fossil fuel is a cause of concern due to global warming issues (Nasri et al., 2014). Adsorption of CO_2 with solid sorbent materials such as activated carbons is attractive due to its wide availability, high thermal stability, low cost, and low sensitivity to moisture (Rashidi et al. 2013). Preparation of highly stable activated carbon that can perform satisfactory at relatively high temperature is desirable (Shafeeyan et al., 2012). Palm shell waste is abundant in Malaysia and South-East Asia, it's found to be good precursor for activated carbon production (Guo et al., 2008). It was observed that PEEK- based porous carbon have excellent properties desirable for high temperature (Cansado et. al. 2009) and gas storage applications (Thomas et al., 2010). This is due to the excellent textural properties of PEEK porous carbons together with its semi-crystalline nature; Based on this, the research focuses on investigation of capacity of hybrid PEEK with sustainable Palm shell porous carbons for CO_2 adsorption application.

Adsorption isotherms describe the equilibrium relationship between solid adsorbent and adsorbate (CO_2). Adsorption isotherms are very important in prediction of adsorption parameters and quantitative comparison of adsorbent behavior under various conditions (Foo and Hameed, 2010). Common isotherms used in modeling gaseous adsorption on porous adsorbents include Langmuir, Sips, Toth, BET, UNILAN, Dubinin–Radushkevich (DR), Dubinin–Astakhov (DA) (Leppajarvi et al., 2012). The main objective of this research was to evaluate the adsorption equilibrium of CO_2 on microwave palm shell-PEEK porous carbons under different conditions of temperature and pressure.

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2. Experimental

2.1 Sorbent Synthesis and CO_2 adsorption test

Raw palm shell was washed and dried at 105 °C for 24 h. Ground palm shells were carbonized in a tubular reactor placed in a furnace to form chars which were later sieved to 0.5-0.85 mm sizes. Granulated Victrex PEEK was also pyrolysed at 800 °C in a furnace to form the PEEK Char (PEKC). The PEEK precursor was heated at the rate of 10 °C/min, under 90 cm^3/min flow of nitrogen gas for 45 min. The resultant PEEK char were sieved to 0.5-0.85 mm sizes. PEEK char (20 and 26 %) was blended with Palm kernel char (PKC) to form palm-PEEK char (PPC). The blended chars were mixed with impregnating agent (K_2CO_3) in the ratio of 1:1. Conditions of sample impregnation, microwave irradiation and application in CO_2 adsorption are given elsewhere (Nasri et al., 2014). The final samples containing 20 and 26 % of PEEK which were irradiated at 400 and 500 W were denoted as M4P2 and M5P2.

2.2 Adsorption Isotherm Modeling

Equilibrium relationships correlate the amount of gas adsorbed on a solid sorbate with the applied gas pressure (adsorption isotherms).

Freundlich adsorption isotherm

Freundlich adsorption isotherm is represented as:

$$q = K_F P^{1/n} \tag{1}$$

Freundlich isotherm is the earliest known relationship describing the non-ideal and reversible adsorption. The empirical model can be applied to multilayer adsorption, with non-uniform distribution of adsorption heat and affinity over the heterogeneous surface (Foo and Hameed, 2010). Where, q_e is the amount of adsorbate adsorbed per unit mass of adsorbent (mmol/g), P is pressure of the CO_2 in the bulk gas phase, $K_F$and $1/n$ are the Freundlich adsorption constant and a measure of adsorption intensity.

Langmuir adsorption isotherm

Langmuir's isotherm assumes monolayer adsorption and that the surface is homogeneous. The adsorption occurs only at finite number of sites that are identical (Granier et al., 2011). Langmuir's isotherm model is express in Eq(2):

$$\Theta = \frac{q}{q_m} = \frac{K_L P}{(1 + K_L P)} \tag{2}$$

Therefore

$$q = \frac{q_m K_L P}{(1 + K_L P)} \tag{3}$$

Where: Ɵ is the occupancy ratio or fractional coverage of the surface, which can be defined as the ratio of the adsorbed mass (q) to the maximum adsorbed mass at monolayer coverage (q_m) (Al-Hajjaj et al., 2011), K_L is the Langmuir constant.

Toths adsorption isotherm

Toth isotherm is a three parameter empirical equation developed to improve the fit of the Langmuir isotherm and to describe heterogeneous adsorption systems with n ≠ 1 (Granier et al., 2011). Toth's equation is represented in Eq(4):

$$\frac{q}{q_m} = \frac{\alpha_T P}{[1 + (\alpha_T P)^n]^{1/n}} \tag{4}$$

Where α_T and n are Toths constants, P is the adsorbate gas pressure at equilibrium (kPa), q_e is the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g or mmol/g).

Sips adsorption isotherm

Sips isotherm is a combination of the Langmuir and Freundlich isotherm type models and expected to describe heterogeneous surfaces much better. At low adsorbate concentrations it reduces to a Freundlich isotherm, while at high adsorbate concentrations it predicts a monolayer adsorption capacity characteristic of the Langmuir isotherm (Shahryari et al., 2010). Sips Model could be written as:

$$q = \frac{q_m K_{LF} P^{1/n_{LF}}}{1 + K_{LF} P^{1/n_{LF}}} \tag{5}$$

K_{LF} is the Sips (L-F) constant which is temperature dependant; n_{LF} is the parameter that characterize the system heterogeneity.

Model Validity and Fitting

The validity of the models to fit the experimental data was evaluated by the root-mean-square deviation (RMSD) in Eq(6) and coefficient of determination (R^2). RSMD is a commonly used statistical tool for measuring the predictive power of a model. RSMD standard equation is defined as:

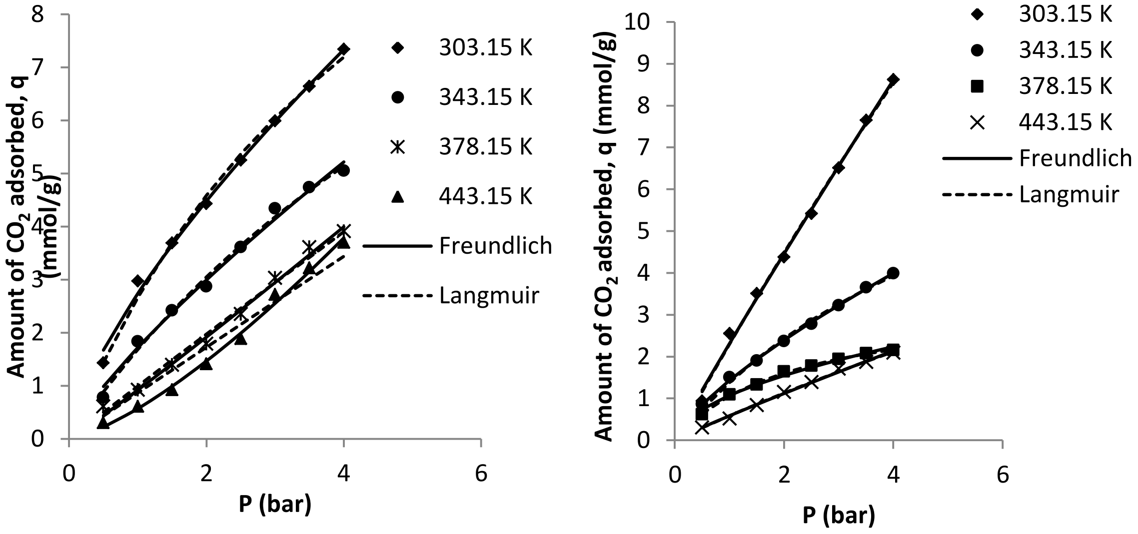
$$RMSD = [1/n\sum(q_{exp} - q_P)^2]^{1/2} \tag{6}$$

The lower the RMSD value the better the estimated model performs. The R^2 represents the percent of the closeness of experimental data to the line of best fit. The coefficient of determination is such that $0 < R^2 < 1$, the more the R^2 is close to 1, the better the model fits the data (Hossain et al., 2013).

3. Results and Discussion

3.1 CO_2 Adsorption Isotherm Modelling

The adsorption isotherm indicates how the adsorbate (CO_2) and adsorbent (porous carbons) interact. Correlation of equilibrium data is vital in design and optimization of sorbent performance (Kaouah et al., 2013). Due to the inherent bias resulting from linearization, alternative isotherm parameter sets were determined by non-linear regression. The adsorption studies were carried out at different initial pressures between 0 to 4 bar at four different temperatures, i.e. 303.15, 343.15, 378.15 and 443.15 K. In this study, 2-parameter Langmuir and Freundlich adsorption isotherms models were applied together with three parameter Sips and Toths models. Effect of temperature and pressure on the CO_2 adsorption capacity of M4P2 and M5P2 was also studied. As depicted in Figure 1 and 2, the amount of CO_2 adsorbed increases with an increase in the pressure of the system. This is due to the fact that increasing the pressure increases the van der Waals attraction forces between the sorbate gas and adsorbent (Maryam et al., 2008). In this study, the highest amount of CO_2 uptake by M4P2 and M5P2 adsorbent obtained were 7.34 and 8.62 mmol/g at 303.15 K and 4 bar (Figure 1).



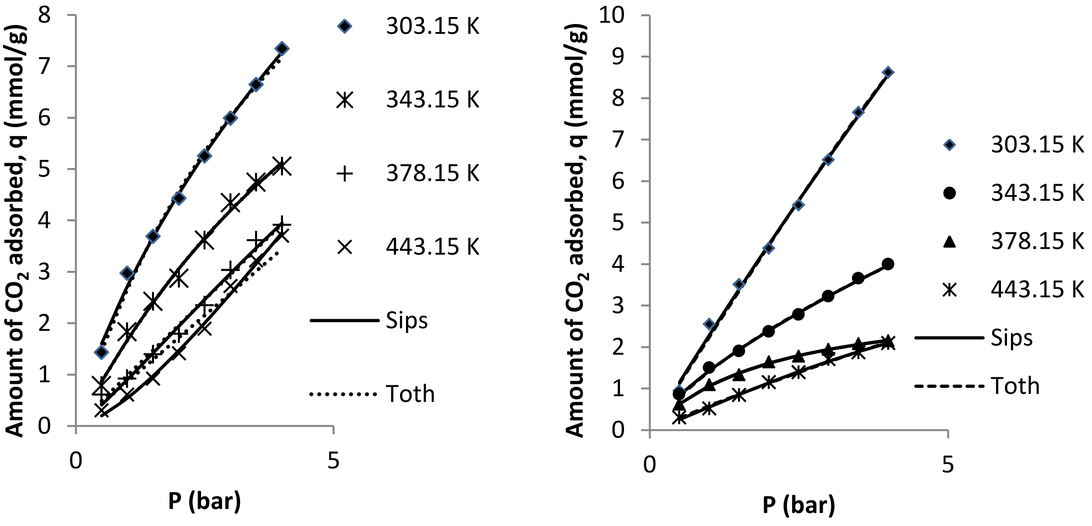
(a) (b)

Figure 1: Equilibrium isotherm of CO_2 adsorption on (a) M4P2 and (b) M5P2 at various temperatures correlated with 2-parameter Freundlich and Langmuir models

The CO_2 uptake isotherm profile is of type 1 according to IUPAC classification of isotherms. Initially, there is drastic increase in CO_2 uptake at lower pressure but then slowly increased with increase in pressure.The plots of the experimental adsorption data and the predicted data from Langmuir and Freundlich isotherm models are shown in Figure 1. The plots for the experimental data with predicted from the three parameter Sips and Toth are also shown in Figure 2. The solid lines represent the Sips isotherm and Freundlich isotherm in the three parameter and two parameter models. The broken lines represent the Toth isotherm and Langmuir isotherm in the three parameter and two parameter models. The detailed isotherm parameters were listed in Table 1 for the two and three parameter models. The Langmuir and

Freundlich isotherm models were valid and exhibited satisfactory fits to the experimental data for M4P2 and M5P2. Both models gave $R^2 > 0.98$ (Table 1) except for M4P2 at 443.15 K, which could be related to the nature of the un-favourable adsorption at high temperature. Low values of RSMD for the Langmuir and Freundlich models for all the samples indicated that the models fit well with the experimental data (Table 1).

For M4P2, n is greater than 1 at 303.15 and 343.15 K but reduced to less than 1 at higher temperatures such as 378.15 and 443.15 K. Freundlich isotherm better described the adsorption for M4P2, the same applies to M5P2 at lower temperatures i.e. 303.15 and 343.15 K (Table 1) than the Langmuir. The Freundlich model is used for heterogeneous systems with interaction between the molecules adsorbed. This indicated that Freundlich isotherm describe the adsorption system better at lower temperatures while the Langmuir isotherm is better at higher temperature. M5P2 exhibited a higher CO_2 adsorption capacity of 8.62 mmmol/g at 4 bar than M4P2 (Figure 1 and 2). This could be due to release of volatiles from the char surface and pore widening (Hu et al., 2001).



(a) (b)

Figure 2: Equilibrium isotherm of CO_2 adsorption on (a) M4P2 and (b) M5P2 at various temperatures correlated with 3-parameter Sips and Toths models

For the three parameter models, both Sips and Toth model fits the CO_2 adsorption data on the PCs well base on R^2 and RSMD values (Table 1). Sips model gives higher correlation coefficient at all temperatures (i.e. 303.15 and 243.15, 378.15 and 443.15 K) than the Toth model. Lower RSMD values also suggest that Sips model fits the experimental data better than the Toth model. This is further elucidated by the fact that the Sips solid line is in close proximity with the experimental data points (Figure 2). The adsorption capacity of all the sorbent decreased with increase in temperature (Figure 1 and 2); the higher the adsorption temperature, the lower the amount of CO_2 adsorption. This is due to the fact that adsorption is exothermic. According to the Le Chatelier's principle, the endothermic desorption will be favoured when temperature increases (Wang et al., 2012). Therefore, less amount of CO_2 is adsorbed at higher temperatures. The affinity constant, b, measures how strong adsorbate molecules are attracted onto a surface. Hence, it seems obvious that CO_2 is strongly attracted to the surface. In an exothermic process like adsorption, b decreases with temperature for all the adsorbates. The parameter n in the sips equation indicates the heterogeneity of the system. The value of n obtained was usually higher at lower temperature (303.15 K) then gradually decreases with increase in temperature. At lower temperature where $n > 1$ (Table 1), suggest some degree of heterogeneity of the gas/ activated carbon system (Gacia et al., 2013). The n parameter from Tóth's model, reflects heterogeneity of the sorbent surface. In most of the results obtained for the PCs sorbents n is not one, which indicated the heterogeneity of the surface which is favourable for adsorption (Vargas et al., 2012).

4. Conclusion

The study demonstrated adsorption of CO_2 on palm shell-PEEK porous carbons. The CO_2 adsorption capacities of the porous carbons were tested by static volumetric method and fitted with 2 and 3-parameter isotherm models. The saturated amounts of CO_2 adsorption on the activated carbons decrease with increase in adsorption temperature but increases with pressure. In all cases, the CO_2 uptake was faster initially and then decrease with increase time. The highest amount of CO_2 uptake by M4P2 and M5P2 adsorbent obtained were 7.34 and 8.62 mmol/g at 303.15 K and 4 bar. Sips adsorption isotherm model fits the data better with higher correlation coefficient and low RSMD at all temperatures.

Table 1: Freundlich, Langmuir, Sips and Toth Isotherm Isotherm and fitting parameters for the adsorption of CO_2 on PCs

Sample	Isotherm	Temperature (K)	n	K_F		R^2	RSMD
M4P2	Freundlich	303.15	1.4061	2.7374	-	0.9957	0.1214
		343.15	1.2480	1.7182	-	0.9909	0.1337
		378.15	0.9438	0.9199	-	0.9919	0.1035
		443.5	0.7311	0.5684	-	0.9941	0.0905
M5P2	Freundlich	303.15	1.0535	2.3103	-	0.9967	0.1404
		343.15	1.3545	1.4330	-	0.9989	0.0333
		378.15	1.8771	1.0684	-	0.9833	0.0641
		443.5	1.0685	0.5840	-	0.9952	0.0419
			q_m	K_L	-		
M4P2	Langmuir	303.15	16.6641	0.1900	-	0.9942	0.1411
		343.15	16.3086	0.1150	-	0.9943	0.1056
		378.15	154.3869	0.0065	-	0.9891	0.1204
		443.15	492.4277	0.0018	-	0.9527	0.2558
M5P2	Langmuir	303.15	93.9679	0.0250	-	0.9966	0.1427
		343.15	10.2349	0.1559	-	0.9940	0.0782
		378.15	3.3104	0.4721	-	0.9977	0.0236
		443.15	17.0392	0.0354	-	0.9963	0.0369
			q_m	b	n		
M4P2	Sips	303.15	38.0024	0.0770	1.2346	0.9961	0.1159
		343.15	12.1808	0.1607	0.9209	0.9949	0.1003
		378.15	21.3716	0.0441	0.8468	0.9903	0.1137
		443.15	28.8275	0.0192	0.6743	0.9942	0.0896
M5P2	Sips	303.15	93.5002	0.0251	0.9959	0.9966	0.1424
		343.15	48.6391	0.0302	1.2853	0.9986	0.0385
		378.15	3.2435	0.4861	0.9807	0.9978	0.0235
		443.15	5.8881	0.1041	0.8293	0.9976	0.0299
			q_m	b	n		
M4P2	Toth	303.15	16.8351	0.1905	0.9773	0.9942	0.1407
		343.15	9.5569	0.1848	1.5140	0.9948	0.1005
		378.15	22.6474	0.0434	5.0122	0.9903	0.1137
		443.15	16.8746	0.0510	6.2766	0.9538	0.2528
M5P2	Toth	303.15	17.8168	0.1258	2.9139	0.9962	0.1513
		343.15	100.3515	0.0272	0.3637	0.9977	0.0485
		378.15	3.2140	0.4736	1.0443	0.9978	0.0235
		443.15	10.6231	0.0557	1.2683	0.9965	0.0358

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