

A SEMI-EMPIRICAL MODEL TO PREDICT ADSORPTION EQUILIBRIUM OF CARBON DIOXIDE ON AMMONIA MODIFIED ACTIVATED CARBON

¹MOHAMMAD SALEH SHAFEEYAN, ²WAN MOHD ASHRI WAN DAUD

^{1,2}Department of Chemical Engineering, Faculty of Engineering, University of Malaya,
50603 Kuala Lumpur, Malaysia
E-mail: ¹ms.shafeeyan@gmail.com, ²ashri@um.edu.my

Abstract- The adsorption equilibria of carbon dioxide on a commercial granular activated carbon (GAC) and an ammonia-modified GAC (OXA-GAC) were investigated over the temperature and pressure range of 303 to 333 K and up to pressures of 1 atm. To distinguish the contribution of chemisorption and physisorption mechanisms to the overall CO₂ adsorption, we developed a semi-empirical equilibrium model. A non-linear regression method was employed to estimate the best fitting parameters corresponding to the isotherm model. An analysis of the calculated statistical parameters indicated that the proposed model successfully fit the experimental data over the entire analyzed ranges of temperature and pressure. The initial isosteric enthalpy of adsorption calculated using the Clausius–Clapeyron equation indicated a sharp increase in CO₂–adsorbent interaction after ammonia modification of the untreated adsorbent, consistent with a dramatic uptake of CO₂ at low partial pressures. The heats of adsorption calculated using the temperature-dependent parameters of the proposed model for physisorption and chemisorption of CO₂ onto the modified adsorbent were in excellent agreement with the heats of adsorption obtained from the experimental data.

Keywords- Activated carbon, Ammonia modification, CO₂ adsorption, Adsorption isotherm, Toth equation, Isosteric enthalpy.

I. INTRODUCTION

Global warming and related environmental damage associated with emissions of CO₂, the most significant greenhouse gas, have long been recognized to represent a potential serious threat to the future of the earth's environment. As a result, various CO₂ separation techniques are currently under investigation [1]. Currently, absorption with amine-based absorbents is the preferred technology for the large-scale separation of CO₂ from the flue-gas streams of fossil-fuel-based power plants. However, this method suffers from several significant drawbacks that impede its implementation. The development of alternative, lower lower-cost, energy-efficient CO₂ removal technologies is therefore important [2].

The separation and purification of gas mixtures by adsorption is a potential option because of its ease of operation, high adsorption capacity, minimal environmental impact, and low cost compared to conventional absorption with liquid solvents [3]. The development of an easily regenerated and durable adsorbent will undoubtedly enhance the competitiveness of adsorptive separation for CO₂ capture in flue-gas applications [4]. Among all adsorbents, activated carbon offers several advantages as a CO₂ adsorbent [5].

The CO₂ adsorption performance of activated carbon is well known to be strongly influenced by modification of the surface chemical properties of the activated carbon. Inspired by the current liquid-phase amine scrubbing technology, researchers have incorporated different basic nitrogen functional groups onto the carbon surface for CO₂ removal from

gaseous mixtures at relatively high temperatures [6]. Several authors have proposed modifying activated carbon with gaseous ammonia as a suitable technique to produce efficient CO₂ adsorbents [7, 8].

The study of the adsorption equilibria is essential in supplying the basic information required for developing and validating models that represent the nature of the adsorption processes. However, as far as we know, very few data have been reported for CO₂ adsorption over ammonia-modified activated carbons. Furthermore, no studies have been conducted to analyze the CO₂ adsorption isotherms over such adsorbents to fit to a proper isotherm model. Therefore, in the present paper, the adsorption equilibria of carbon dioxide over the parent GAC and its ammonia-modified counterpart (OXA-GAC) at various operating conditions were obtained and used to fit to an appropriate semi-empirical isotherm model.

II. DETAILS EXPERIMENTAL

2.1. Adsorbent materials

The modified adsorbent (a pre-oxidized sample that was aminated at 425 °C for 2.12 h), referred to as OXA-GAC, was used as a starting material. The commercial granular palm-shell-based activated carbon (referred to as GAC) evaluated in the present paper was obtained from Bravo Green Sdn Bhd (Malaysia).

2.2. CO₂ adsorption measurements

CO₂ adsorption isotherms of the modified and untreated activated carbon samples were measured using a Micromeritics ASAP 2020 instrument. The

equilibrium experiments were conducted at temperatures of 30, 45 and 60 °C and at pressures up to 102 kPa.

2.3. Adsorption isotherm equations

For each modified and untreated activated carbon adsorbent, three isotherms were measured at 30, 45, and 60 °C and at pressures up to 102 kPa. Three different pure-species isotherm models—the Freundlich (Eq. 1), Sips (Eq. 2), and Toth (Eq. 3) isotherm equations—were used to correlate experimental equilibrium results.

$$q = K_F P^{1/m_F} \quad (1)$$

$$q = \frac{q_m (K_S P)^{1/m_S}}{1 + (K_S P)^{1/m_S}} \quad (2)$$

$$q = \frac{q_m K_T P}{(1 + (K_T P)^{m_T})^{1/m_T}} \quad (3)$$

In Eqs. 1-3, q represents the adsorbed concentration, P is the equilibrium pressure, q_m is the maximum loading capacity, K_i is the equilibrium constant (K_F) or the affinity parameter (K_S and K_T), and m_i (m_F , m_S , and m_T) is the parameter that refers to the system heterogeneity.

In the current study, the parameters of the isotherm equations for each temperature were obtained by non-linear regression analysis. To quantify and compare the goodness of fit of the above isotherm models to the experimental data and adjust each set of isotherm constants, two different error functions, the average relative error (ARE) and nonlinear regression coefficient (R^2), were evaluated.

III. RESULTS AND DISCUSSION

3.1. Adsorption equilibrium study

Adsorption isotherms obtained at temperatures of 30, 45 and 60 °C and at pressures up to 102 kPa for the ammonia-modified and untreated carbon are graphically represented in Figs. 1a and b, respectively. As evident in these figures, for both modified and unmodified adsorbent, the concentration of adsorbed CO₂ increases with increasing pressure. For the unmodified adsorbent, CO₂ capture with a pure physisorption process was proposed as a controlling mechanism. As evident in Figs. 1a and b, in comparison with the unmodified adsorbent, OXA-GAC exhibited a higher CO₂ uptake, particularly at low partial pressures, as reflected by the steep initial slope of the isotherms. This enhanced uptake stems from adsorption by the nitrogen functional groups in addition to CO₂ capture by physical adsorption [9]. At low CO₂ partial pressures, the contribution of chemisorption to the

total CO₂ uptake is more pronounced, whereas physisorption within the pores becomes significant at higher concentrations.

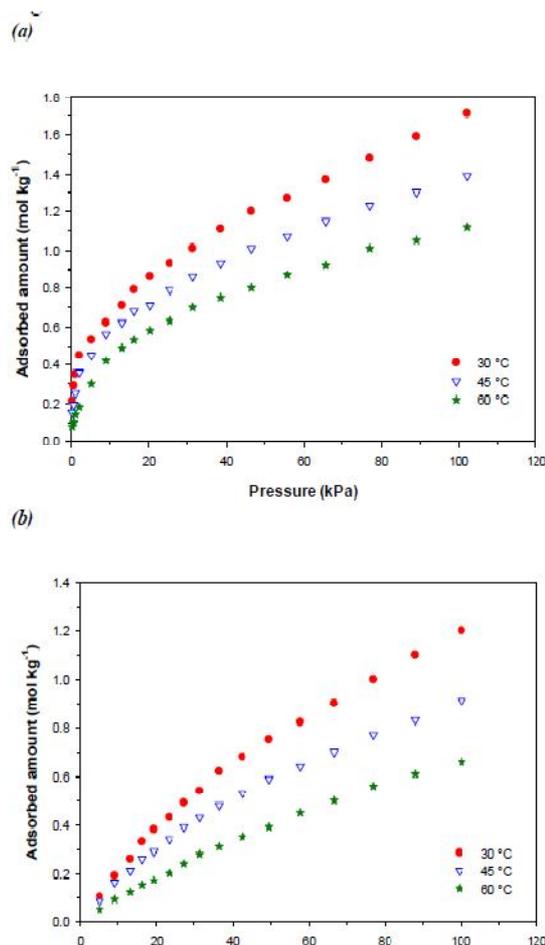


Fig.1. (a & b) Experimental adsorption isotherms of CO₂ on (a) modified and (b) untreated activated carbon measured at 30, 45 and 60 °C.

As evident in the figures, the CO₂ adsorption was strongly dependent on the nitrogen functionalities: OXA-GAC exhibited a higher uptake than GAC over the whole pressure range studied. Moreover, as shown in Figs. 1a and b, both of the adsorbents adsorbed less CO₂ at 45 and 60 °C than at 30 °C. The observed decrease in CO₂ uptakes at higher temperatures is attributed to the exothermic nature of the adsorption process, where both the molecular diffusion rate and the surface adsorption energy increase with increasing temperature [10]. However, interestingly, the results at 40 °C and especially at 60 °C indicate that, compared to the unmodified adsorbent, OXA-GAC exhibited a smaller decrease in the amount adsorbed with increasing temperature. The modified adsorbent did exhibit a decrease in the amount adsorbed with increasing temperature; however, this decrease was not as pronounced as the uptake reduction observed for GAC, where physisorption is the only retention phenomenon. Because in the high-temperature adsorption, the contribution of chemisorption to the total adsorption

is more significant; a possible explanation for this observation is the occurrence of strong chemical reactions between CO₂ and incorporated nitrogen-functionalities on the surface.

3.2. Equilibrium isotherm modeling

As previously suggested, the overall CO₂ adsorption on the ammonia-modified activated carbon could be the result of both physical adsorption within the pores and chemical adsorption onto the nitrogen surface groups. Distinguishing between these two mechanisms is useful in identifying the factors that may affect the rate of the adsorption process [4]. Therefore, in the present study, we implemented an approach that takes into account the physical adsorption as well as the enhanced adsorption due to chemical interactions. A semi-empirical model that considers the simultaneous occurrence of two independent chemical and physical adsorption mechanisms for CO₂ adsorption can be expressed as the following equation:

$$q = q_{chem} + q_{phys} \quad (4)$$

where q is the overall adsorption of CO₂ on ammonia-modified activated carbon, q_{chem} represents the CO₂ uptake by nitrogen functionalities and q_{phys} denotes the physical adsorption onto the porous structure.

To differentiate the contribution of each independent mechanism to the total adsorption capacity of the modified adsorbent, a procedure was used to calculate

q_{phys} on the basis of the CO₂ adsorption data for the untreated activated carbon adsorbent. In our previous study, we demonstrated that, under the conditions used for the modification of the adsorbent, the ammonia treatment did not significantly alter the pore structure of the studied adsorbent [11]. Given that the amount of physical adsorption is proportional to the adsorbent textural properties, the difference in the amount of CO₂ physisorbed onto both modified and untreated activated carbon under the same operating conditions is reasonably assumed to be almost negligible. Therefore, the contribution from chemical adsorption (q_{chem}) to the total CO₂ uptake is estimated

by subtracting the amount of q_{phys} for the untreated adsorbent from the overall adsorption uptake (q), measured experimentally for the modified sample. Accordingly, using the equilibrium adsorption data for GAC, and subtracting the measured contribution of physisorption from the overall uptake, the corresponding values of q_{chem} for OXA-GAC at different temperatures were calculated; the results are represented in Fig. 2.

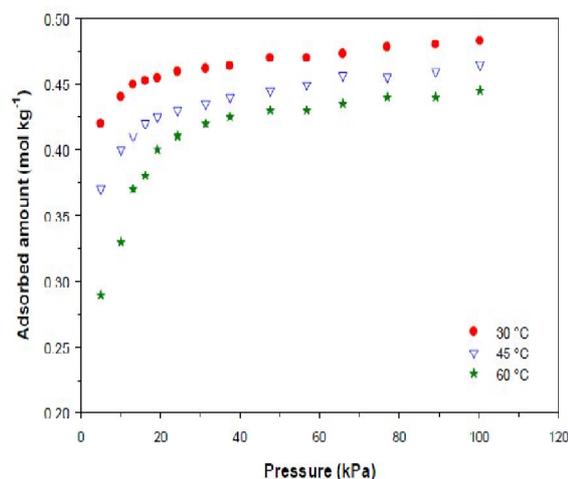


Fig.2. Calculated adsorption isotherms for CO₂ chemisorption onto the modified adsorbent at 30, 45 and 60 °C.

Applying various conventional isotherm models, we can express the terms on the right side of Eq. (4) in different forms to describe each of the mechanisms with a proper isotherm model. Accordingly, Freundlich, Sips and Toth isotherm models were employed in this work. The optimal values of the Freundlich, Sips and Toth isotherm parameters are summarized in Tables 1-3, respectively.

Table1: Freundlich isotherm parameters with R^2 and ARE for each independent mechanism at temperatures of 303, 318, and 333 K

	Temperatures		
	303 K	318 K	333 K
<i>Physical adsorption</i>			
K_f ($\text{mol kg}^{-1} \text{kPa}^{-1/m_f}$)	1.22	0.93	0.61
m_f (dimensionless)	2.45	2.15	1.74
R^2	0.996	0.995	0.996
ARE (%)	5.56	5.95	5.02
<i>Chemical adsorption</i>			
K_f ($\text{mol kg}^{-1} \text{kPa}^{-1/m_f}$)	0.38	0.16	0.06
m_f (dimensionless)	4.66	4.14	3.81
R^2	0.957	0.968	0.808
ARE (%)	0.59	0.83	5.16

To quantitatively compare the quality of the nonlinear regressions for these three models, the average relative error (ARE) and nonlinear regression coefficient (R^2) were calculated; the results are included in Tables 1-3. The higher values of K_f obtained for the physisorption mechanism indicated greater adsorption compared to chemisorption, whereas the higher values of m_f observed for chemisorption denoted a more favorable adsorption and a stronger bond between CO₂ and the modified

adsorbent ($1 < m_f < 10$). The heterogeneity of the adsorbent surface can also be described with the exponent m_i in the Sips and Toth isotherm equations [12]. When the surface is homogeneous, m_i is equal to unity and the isotherm expressions reduce to the Langmuir equation.

Table2: Sips isotherm parameters with R^2 and ARE for each independent mechanism at temperatures of 303, 318, and 333 K

	Temperatures		
	303 K	318 K	333 K
<i>Physical adsorption</i>			
q_m (mol kg^{-1})	3.43	2.12	1.76
K_s (kPa^{-1})	0.69	0.39	0.23
m_s (dimensionless)	1.11	1.08	0.98
R^2	0.998	0.998	0.999
ARE (%)	2.93	2.08	1.71
<i>Chemical adsorption</i>			
q_m (mol kg^{-1})	0.53	0.48	0.44
K_s (kPa^{-1})	8.73×10^2	1.96×10^2	50.76
m_s (dimensionless)	2.12	2.02	1.83
R^2	0.970	0.981	0.991
ARE (%)	0.54	0.67	0.99

In agreement with the Freundlich model, the obtained values of the surface heterogeneity parameter in the Toth ($m_t < 1$) and Sips ($m_s > 1$) equations showed a higher degree of heterogeneous adsorption for CO₂ chemisorption. From Tables 2 and 3, the values of the saturation capacity parameter (q_m), which indicate the maximum amount that can possibly be adsorbed, decreased with increasing temperature. The observed decrease is associated with the exothermicity of the adsorption process [13]. On the basis of the calculated values of ARE and R^2 tabulated in Tables 1-3, both the Sips and Toth isotherms were capable of fitting the equilibrium data over a broad range of experimental conditions. However, the Toth equation, which involves asymmetrical quasi-Gaussian distribution of adsorption sites, provided a slightly better fit. The low values obtained for the ARE, as well as the high values of the nonlinear regression coefficient, indicate the goodness of the fit. Therefore, compared to the Freundlich and Sips models, the Toth equation is more accurate and more capable of describing the CO₂ adsorption isotherms over the ammonia-modified adsorbent. Thus, only the

Toth model was used here to illustrate the quality of its fit to the experimental equilibrium data (Fig. 3).

Table3: Toth isotherm parameters with R^2 and ARE for each independent mechanism at temperatures of 303, 318, and 333 K

	Temperatures		
	303 K	318 K	333 K
<i>Physical adsorption</i>			
q_m (mol kg^{-1})	5.50	2.83	1.46
K_t (kPa^{-1})	0.91	0.59	0.40
m_t (dimensionless)	0.59	0.63	0.68
R^2	0.999	0.999	0.999
ARE (%)	2.65	2.01	1.65
<i>Chemical adsorption</i>			
q_m (mol kg^{-1})	0.54	0.49	0.46
K_t (kPa^{-1})	1.05×10^5	2.94×10^4	9.20×10^3
m_t (dimensionless)	0.29	0.30	0.31
R^2	0.971	0.982	0.992
ARE (%)	0.52	0.64	0.93

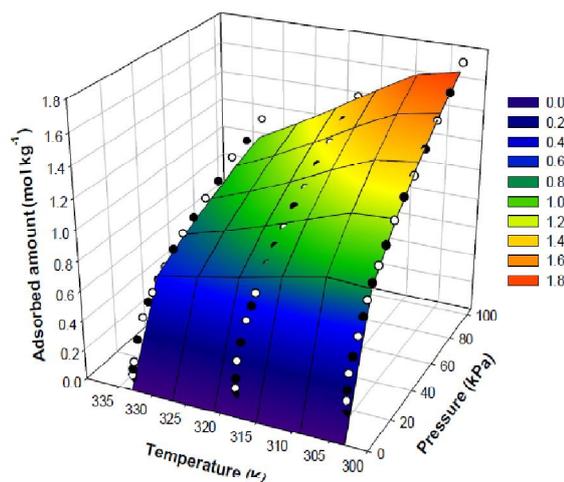


Fig.3. Graphical evaluation of the fit of the experimental equilibrium data to the proposed model for the modified adsorbent, whose parameters are presented in Tables 4 & 5. The surface is the global isotherm model, and the black and white circles show the experimental data at 303, 318 & 333 K.

The complete form of the proposed semi-empirical model is expressed as follows:

$$q = \left[\frac{q_m K_t P}{(1 + (K_t P)^{m_t})^{1/m_t}} \right]_{phys} + \left[\frac{q_m K_t P}{(1 + (K_t P)^{m_t})^{1/m_t}} \right]_{chem} \quad (5)$$

where the subscripts "phys" and "chem" indicate the contributions of each independent mechanism to the total CO₂ uptake. To express the temperature dependence of the Toth isotherm parameters for the purpose of interpolating or extrapolating the equilibrium data to various temperatures, as well as determining the isosteric enthalpy of adsorption, the

parameters, K_i , q_m and m_i are described by the following equations [14]:

$$K_i = K_{i_0} \exp \left[-\frac{\Delta H}{RT_0} \left(\frac{T_0 - T}{T} \right) \right] \quad (6)$$

$$q_m = q_{m_0} \exp \left[\eta \left(\frac{T_0 - T}{T_0} \right) \right] \quad (7)$$

$$m_i = m_{i_0} + \alpha \left(\frac{T - T_0}{T} \right) \quad (8)$$

The optimal parameter values for both the chemical and physical adsorption mechanisms were obtained by nonlinear regression; the results are presented in Table 4. The surface obtained from the global fitting of the aforementioned model to the experimental data (Fig. 3) shows that the equilibrium data are described well for all temperatures when the adsorption isotherm plotted according to the proposed Toth equation is used.

Table4: Optimal values of the proposed Toth temperature-dependent parameters

	α	η	$(-\Delta H)$
	(dimensionless)	(dimensionless)	(kJ mol ⁻¹)
Physical adsorption	0.96	13.43	23.05
Chemical adsorption	0.25	1.67	68.11

3.3. Isotheric heat of adsorption

The isotheric heat of adsorption, Q_{st} , also denoted as $-\Delta H$ (kJ mol⁻¹), at a specific adsorbate loading can be estimated using the Clausius–Clapeyron equation as follows [15]:

$$-\frac{Q_{st}}{R} = \left(\frac{\partial \ln P}{\partial (1/T)} \right)_{q^a} \quad (9)$$

where q^a is a specific surface loading (mol kg⁻¹).

The isotheric heat is independent of the surface coverage when no interaction occurs between adsorbed molecules, and the surface is energetically homogeneous. However, a variation of the isotheric heats with the surface loading indicates the existence of different levels of surface energy and heterogeneity of the adsorbent surface [13]. Figure 4 depicts the variation of Q_{st} (calculated using the Clausius–Clapeyron equation) as a function of the amount of CO₂ adsorbed for the OXA-GAC and GAC adsorbents. As evident in the figure, the unmodified adsorbent exhibited approximately constant values of Q_{st} for different CO₂ loadings,

indicating the uniform nature of the adsorbent surface. Notably, the obtained initial heat of adsorption for GAC (25 kJ mol⁻¹) corresponds closely to the value of $-\Delta H$ (23 kJ mol⁻¹) calculated from the temperature-dependent parameters of the

proposed model for q_{phys} and is also of the same order of magnitude as the typical values for commercial activated carbon reported in the literature [1, 12]. In contrast, OXA-GAC exhibited rather high values of Q_{st} at the low range of loading, which reflects the relatively strong chemical interactions between CO₂ and the basic nitrogen functionalities.

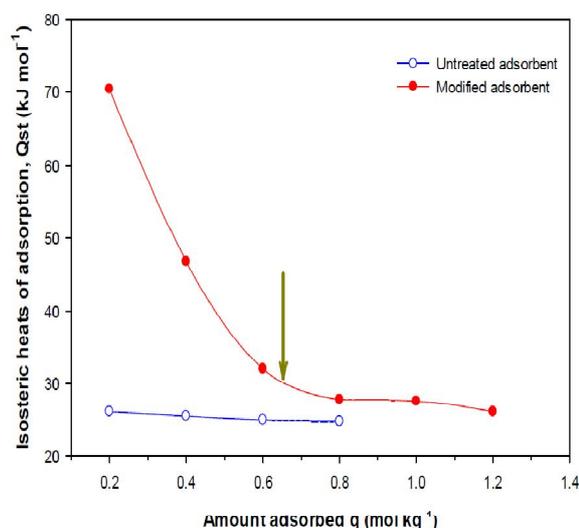


Fig.4. Concentration dependence of the isotheric enthalpy for CO₂ adsorption on the GAC and the OXA-GAC

The isotheric enthalpy of adsorption over OXA-GAC decreases with increasing CO₂ surface loading until it approaches values similar to those of the untreated carbon adsorbent. The observed decrease with increasing loading is attributed to the high degree of heterogeneity of the adsorbent surface [9]. The observed heats of adsorption for the ammonia-modified adsorbent clearly demonstrate the strong and weak interactions of the nitrogen surface groups with CO₂ at low and high coverages, respectively.

Notably, the Q_{st} value obtained at low coverage (70.4 kJ mol⁻¹) is consistent with the value calculated from the proposed Toth parameter K_i for q_{chem} (68.1 kJ mol⁻¹) at zero loading and is in the range of values for typical cases of CO₂ chemisorption (60 to 90 kJ mol⁻¹) [16]. In addition, in agreement with the observed inflection in the isotherms for CO₂ adsorption over the OXA-GAC adsorbent (see Fig. 1a), a corresponding curvature in the plot of the isotheric heat vs. coverage was detected, coinciding with the saturation of the most active adsorption sites (indicated by an arrow in Fig. 4). The observed variation of the slope of the Q_{st} vs. CO₂ loading curve

clearly reflects the occurrence of two independent adsorption mechanisms.

CONCLUSIONS

The equilibrium adsorption isotherms of carbon dioxide on the GAC the OXA-GAC were measured. CO₂ adsorption measurements were performed at three different temperatures (303, 318, and 333 K), and pressures up to 1 atm. The obtained equilibrium data were fitted to the Freundlich, Sips, and Toth isotherms using a semi-empirical approach to differentiate the contributions of physical and chemical adsorption to the total CO₂ uptake. The isotherm parameters were determined independently for each mechanism by non-linear regression. The Toth semi-empirical equilibrium model provided the best fit to the experimental data, with average relative errors of less than 3% observed at all temperatures. The isosteric heats of CO₂ adsorption onto the ammonia-modified adsorbent and onto the untreated adsorbent were determined using the Clausius–Clapeyron equation. The loading dependence of the isosteric enthalpy of CO₂ adsorption over the OXA-GAC reflected an energetic heterogeneity of the adsorbent surface. The initial isosteric heats of adsorption of 70.5 kJ mol⁻¹ and 25.5 kJ mol⁻¹ correspond to the adsorption of CO₂ on the modified and untreated adsorbents, respectively.

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