

Equilibrium Modeling of Carbon Dioxide Adsorption on Zeolites

Alireza Behvandi, Somaveh Tourani

Abstract—High pressure adsorption of carbon dioxide on zeolite 13X was investigated in the pressure range (0 to 4) Mpa and temperatures 298, 308 and 323K. The data fitting is accomplished with the Toth, UNILAN, Dubinin-Astakhov and virial adsorption models which are generally used for micro porous adsorbents such as zeolites. Comparison with experimental data from the literature indicated that the virial model would best determine results. These results may be partly attributed to the flexibility of the virial model which can accommodate as many constants as the data warrants.

Keywords—adsorption models, zeolite, carbon dioxide

I. INTRODUCTION

Fossil fuels supply more than 98% of the world's energy needs. However, the combustion of fossil fuels is one of the major sources of green house gas CO_2 . It is necessary to develop technologies that will allow us to utilize the fossil fuels while reducing the emissions of green house gases. Commercial CO_2 capture technology that exist today is very expensive and energy intensive. Improved technologies for CO_2 capture are necessary to achieve low energy penalties. Pressure swing adsorption (PSA) is one of the potential techniques that could be applicable for removal of CO_2 from high pressure gas streams. PSA processes are based on preferential adsorption of desired gas (e.g. CO_2) on porous materials at a high pressure. To design pressure-swing adsorption (PSA) processes, the basic information required is the adsorption equilibrium behavior of pure components.

In this work, we show the popular adsorption isotherm models such as Toth, UNILAN, Dubinin-Astakhov and virial models for CO_2 on 13X zeolites at temperatures ranging from 298 to 323 K and pressure ranging from 0 to 4 Mpa (4000 kpa). It is found that virial model and Dubinin-Astakhov model are the best and worst models respectively. The best agreement virial equation is due to flexibility of the virial model which can include many constants but in the case of Dubinin's equation, the estimation of the saturated vapor pressure under supercritical condition leads to high uncertainties in data analysis.

II. TRADITIONAL ADSORPTION MODELS

Traditional adsorption models such as those of Langmuir [1], Sips [2], Toth [3], UNILAN [4,5] and Dubinin-Astakhov [6-8] have often been used by some authors to correlate experimental data for equilibrium adsorption isotherms in zeolites.

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We summarized some adsorption models that have been successfully used to fit adsorption isotherm data for zeolites in Table 1. The Langmuir model is capable of fitting the adsorption isotherms of Argon and Krypton in Sodalite [9], some aromatic hydrocarbons in zeolite NaX [10], some branched and cyclic hydrocarbons in silicalite [11], and Argon and Oxygen in zeolite 5A [12]. The Sips model is capable of fitting the adsorption isotherms of Nitrogen in zeolite 5A [13] and Carbon dioxide in zeolites NaX, NiX and CrX [14]. The Toth model is capable of fitting the adsorption isotherms of Nitrogen, Oxygen, and Carbon monoxide in zeolite 10X [15], Carbon dioxide and Hydrogen sulfide in H-mordenite [15]. The UNILAN model is capable of fitting the adsorption isotherms of Oxygen in zeolite 13X [15], and Hydrogen sulfide and Propane in H-mordenite [15]. The Dubinin-Astakhov model is capable of fitting the adsorption isotherms of Methane in zeolite [6], Carbon dioxide in erionite [6], and cyclohexane and n-hexane in zeolite NaX [7, 8].

By considering that the total isotherm is given by sum of two terms of the same form as that given in Table 1 for the Dubinin-Astakhov model (each term with its own adjustable parameters C_s, E , and n), it is possible to fit the adsorption isotherm of carbon dioxide in zeolite 13X. In the above equations isosteric heat (H_{st}) of adsorption at zero loading is determined by following equation:

$$b = b_i^0 \exp\left(\frac{-H_{st}}{RT}\right) \quad (1)$$

When the equilibrium-adsorption isotherm of carbon dioxide in zeolite 13X (shown in fig.1) are displayed with the pressure axis in linear scale, they resemble the type I isotherms in BDDT classification. Therefore, use of traditional models to fit those isotherms looks appealing. By using Cavenati's experimental data [16] and Marquadt's least-square method of non-linear regression, we tried to fit the traditional models of Table 1 to the experimental adsorption isotherm data plotted in fig.1. The resulting fits are shown in figs 2 and 3.

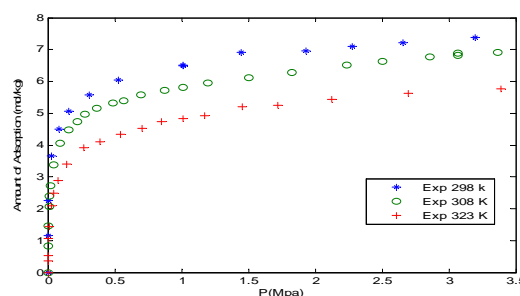


Fig. 1 Experimental adsorption data of Carbon dioxide on zeolite 13X

TABLE I
TRADITIONAL ADSORPTION MODELS THAT HAVE BEEN SUCCESSFULLY USED TO FIT ADSORPTION ISOTHERMS DATA FOR ZEOLITES

Model	Equation	Adjustable parameter
Langmuir	$\frac{C}{C_s} = \frac{bP}{bP + 1}$	C_s, b
Sips	$\frac{C}{C_s} = \frac{(bP)^{1/n}}{1 + (bP)^{1/n}}$	C_s, b, n
Toth	$\frac{C}{C_s} = \frac{(bP)}{(1 + (bP)^n)^{1/n}}$	C_s, b, n
UNILAN	$\frac{C}{C_s} = \frac{1}{2n} \ln \left[\frac{1 + bP \cdot \exp(n)}{1 + bP \cdot \exp(-n)} \right]$	C_s, b, n
Dubinin-Astakhov	$\frac{C}{C_s} = \exp \left\{ - \left[\frac{RT}{E} \ln \left(\frac{P^{sat}}{P} \right) \right]^n \right\}$	C_s, E, n

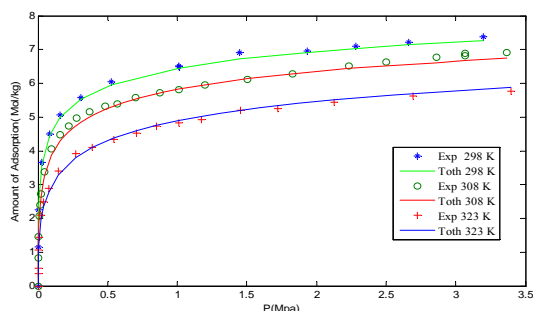


Fig. 2 Fit of the Toth model to the equilibrium adsorption isotherm of Carbon dioxide in zeolite 13X

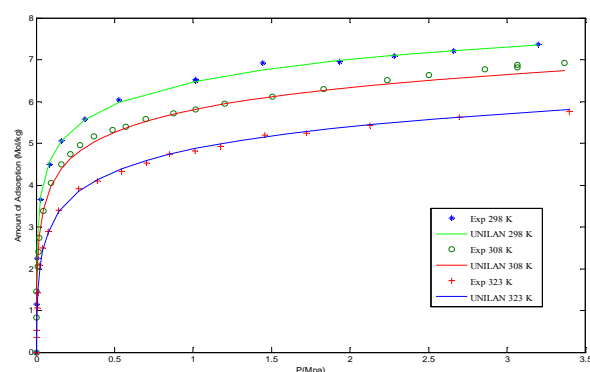


Fig. 3 Fit of the UNILAN model to the equilibrium adsorption isotherm of Carbon dioxide in zeolite 13X

Fitting of Toth, UNILAN equations to experimental data was done with MATLAB program. The best fitting parameters were found by minimizing the objective function, square of residuals F_{obj} .

$$F_{obj} = \sum_{T=1}^3 \sum_{P=0}^{P_{max}} \sum_{S=1}^n (C_{exp} - C_{calc})^2 \quad (2)$$

Where T_i is the three different temperatures used, P_{max} is the maximum pressure of each isotherm, and S is the number of point per isotherm per gas. The Values of fitting parameters are given in Tables II and III.

TABLE II
OPTIMUM VALUES OF THE ADJUSTABLE PARAMETERS C_s, B, N AND THE OBJECTIVE FUNCTION F_{obj} FOR THE FIT OF THE TOTH MODEL TO THE EQUILIBRIUM ADSORPTION ISOTHERMS OF E CARBON IN ZEOLITE 13X

C_s (mol/kg)	n	b_0 (MPa ⁻¹)	H_{st} (j/mol)	F_{obj}
10.9946	0.2303	8.2287e-8	-6.2212e4	0.39

TABLE III
OPTIMUM VALUES OF THE ADJUSTABLE PARAMETERS C_s, B, N AND THE OBJECTIVE FUNCTION F_{obj} FOR THE FIT OF THE UNILAN MODEL TO THE EQUILIBRIUM ADSORPTION ISOTHERMS OF CARBON DIOXIDE IN ZEOLITE 13X

C_s (mol/kg)	n	b_0 (MPa ⁻¹)	H_{st} (j/mol)	F_{obj}
9.8568	6.3367	1.4716e-11	-6.6756e4	0.41

Dubinin's equation was also used to fit the data. Although this method is commonly used in high pressure adsorption, the agreement was not nearly as good as the obtained from the Toth and UNILAN models. These results may be partly attributed to the estimation and extrapolated the reduced Kirchhoff's equation to obtain "saturation Pressure" whenever the temperature is above T_c . The uncertainty in P_s is also observed by the DA parameters. Fig 4 shows a representative DA fitting of these data. The DA parameter also is shown in Table IV.

TABLE IV
OPTIMUM VALUES OF THE ADJUSTABLE PARAMETER C_s, E, N AND THE OBJECTIVE FUNCTION F_{obj} FOR THE FIT OF THE DUBININ-ASTAKHOV MODEL TO THE EQUILIBRIUM ADSORPTION ISOTHERMS OF CARBON DIOXIDE IN ZEOLITE 13X

C_s (mol/kg)	n	E (j/mol)	F_{obj}
7.281	1.5976	1.5321e4	1.7

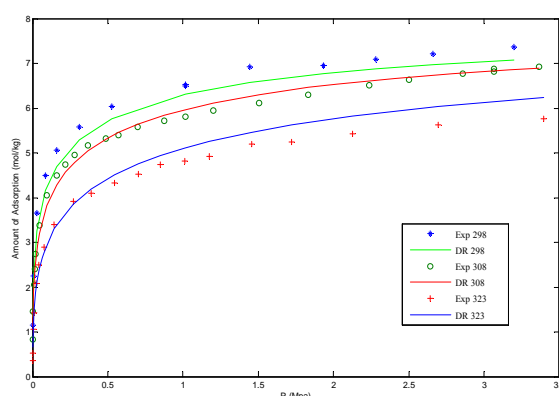


Fig. 4 Fit of the DR model to the equilibrium adsorption isotherm of Carbon dioxide in zeolite 13X

III. THE VIRIAL ADSORPTION MODEL

Among various traditional isotherm models tested, the virial equation [16] gave the best fit to data. The general form of the model is given by eq (3).

$$P = N \exp[K(T) + B(T)N + C(T)N^2 + D(T)N^3 + \dots] \quad (3)$$

Where $K(T)$ is the exponential Henry's law constant related to adsorbate - adsorbent interactions, and $B(T)$, $C(T)$, and $D(T)$ stand for the two body, and four body interactions in the adsorbed phase, respectively. The virial coefficients can be expanded in inverse temperature as follows.

$$\ln\left(\frac{P}{N}\right) = K_0 + \frac{K_1}{T} + \left(\frac{B_1}{T} + \frac{B_2}{T^2} + \frac{B_3}{T^3} + \dots\right)N + \left(\frac{C_1}{T} + \frac{C_2}{T^2} + \frac{C_3}{T^3} + \dots\right)N^2 + \dots \quad (4)$$

A stepwise linear regression technique, which maximized the F_{obj} statistic, was employed in fitting the experimental isotherms. Parameters obtained are listed in Table 5. It is interesting to note that only the first term in the inverse temperature series expansion for virial coefficients were significant in all cases.

TABLE V

OPTIMUM VALUES OF THE ADJUSTABLE PARAMETERS K_0, K_1, B_1, C_1, D_1 AND THE OBJECTIVE FUNCTION F_{OBJ} FOR THE FIT OF THE VIRIAL MODEL TO THE EQUILIBRIUM ADSORPTION ISOTHERMS OF CARBON DIOXIDE IN ZEOLITE 13X

K_0	K_1	B_1	C_1	D_1	Hst (j/mol)	F_{obj}
26.48	-1.1062e4	5.25e2	-33.1948	2.1246	-6.2e4	0.36

This might be due to the small temperature range utilized in this study. Fig 5 shows a typical data fit. It is found that the virial model gives the best fit at low and medium pressure range. As expected, small discrepancies are found at high-pressure region, which reflect the limitation of the virial equation of state.

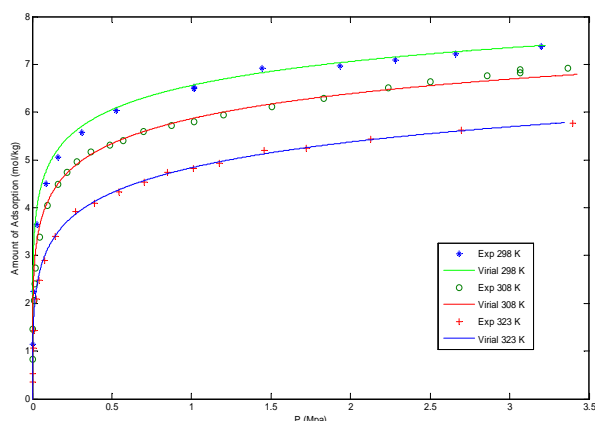


Fig. 5 Fit of the Virial model to the equilibrium adsorption isotherm of Carbon dioxide in zeolite 13X

IV. CONCLUSION

High pressure adsorption of carbon dioxide on zeolite 13X is modeled by isotherms Toth, UNILAN, Dubinin-Astakhov and virial equations. The results show that the Toth, UNILAN and virial models were found to provide a good correlation of all adsorption data. The uncertainty in estimation of P^{sat} when the temperature is above the T_c , leads to this fact that the Dobinin-Astakhov model is incapable for correlating the available equilibrium adsorption isotherm of carbon dioxide in zeolite 13X.

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