Statistical Modeling of Adsorption and Selectivity of the Binary Gases of CO_2/CH_4, CH_4/H_2 and CO_2/H_2 on MWCNT-OH

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Abstract:

Equilibrium adsorption property of multi-walled carbon nanotubes with OH group was studied using experimental design for the adsorption of CO_2, CH_4 and H_2. The effect of temperature, pressure, their binary interactions and quadratic terms were studied for adsorption capacity of nanotubes and the results were analyzed by the face centered central composite design method and analysis of variance. The static experiments were carried out at various temperatures (288.15, 298.15 and 308.15 K) and pressures (4.50, 16.65 and 28.80 bars) in a volumetric apparatus to find out the effective parameters on adsorption capacities of each gas. In addition, influence of effective parameters was studied on CO_2/CH_4, CO_2/H_2 and CH_4/H_2 selectivity of nanotubes in order to realize the capability of this kind of adsorbent for separation processes. Finally, the optimal conditions to maximize CO_2/CH_4, CO_2/H_2 and CH_4/H_2 selectivity were determined.

Keywords: *Design of experiment (DOE), Face centered central composite design, MWCNs, Light gas adsorption*

1. INTRODUCTION

Nowadays a significant growth can be realized in development of technologies related to the separation of gaseous species because of the great demand for purified natural gas, purified hydrogen and other gases for industrial and pharmaceutical applications [1]. On the other hand, green house effect is the most important environmental problem which is caused climate change such as global warming. Emission of greenhouse gases, such as carbon dioxide and methane, into the environment receives the world's concern because of its responsibility for the ever-increasing globe temperature and the weather disasters, therefore capture of greenhouse gases is an urgent task of the world in recent years [2]. Capturing CO_2 by replacement with methane in the landfill gas reservoirs is one of the major tasks of the gas adsorption technologies and it is under survey in many countries such as Astralia. Separation of Carbon dioxide from methane is another important issue for increasing the heat content of natural gas used as fuel in industries [3]. Separation of CO_2 from CH_4, using adsorption process, at ambient temperature using nanoadsorbent and nanoporous materials is favored in the recent years [4]. Adsorption of CO_2 and CH_4 has been investigated using various molecular sieves such as, zeolites, zeotypes and carbon molecular sieves [5-9], although less information has been found around carbon nanotubes [10-11].

Hydrogen preparation is one of the most important issues for the refineries plant applications. CO_2 and CH_4 are the two main impurities accompanied with hydrogen in hydrogen production plants such as methane reforming and naphtha reforming. The selective removal of carbon dioxide from syn- gas is an important and critical process because of poisoning properties of carbon dioxide in presence of water on the surface of the ammonia plant catalysts [2, 12]. Dapeng et al. studied capability of activated carbon for separation of CO_2 from hydrogen by adsorption, and they reported a selectivity of 90 for CO_2/H_2 at room temperature [13].

In methane reforming process, hydrogen with both impurities of methane and carbon dioxide can be recognized in the outlet gaseous product. Impurities are believed to cause various problems in the fuel cell designs, such as catalyst poisoning and membrane failure. In these cases, additional process steps would be required to purify hydrogen as much as possible to meet industrial quality standards. As a result, study and investigation of new materials for high selective adsorption of CO_2 and CH_4 from hydrogen is very important for purification of hydrogen streams [2, 14]. Since the discovery of carbon nanotubes (CNTs) in 1993, this new kind of materials has demonstrated a potential to make a major contribution to a variety of nanotechnology applications, including molecular electronics, gas storage media, and scanning probe microscope tips. Carbon nanotubes might be a good candidate as one of the new adsorbent for CO_2/CH_4, CH_4/H_2 and CO_2/H_2 separation [10]. Temperature and pressure are the most effective variables that might change the gas adsorption capacity and selectivity [15]. Exploring the new materials, such as MWCNTs, requires experimental analysis for their application in the field of the adsorption and separation processes for determination of their properties such as equilibrium adsorption capacity and selectivity as a function of operational pressure and temperature.

In the present work, equilibrium adsorbed carbon dioxide, methane and hydrogen is measured at three levels of temperature and pressure. The face centered central composite experimental design has been applied to the test runs and the results are analyzed statistically. The proper model of adsorption is derived on the base of statistically significant effects of temperature and pressure and finally the optimal conditions for maximizing CO_2/CH_4, CO_2/H_2 and CH_4/H_2 selectivity is determined.

2. EXPERIMENTAL

2.1. Adsorbent

Since the discovery of carbon nanotubes, they have inspired scientists to consider them for a range of potential applications and have become one of the promising adsorbents for gas separation. The rapid development of nanomaterials has provided an opportunity for the application of gas separation. Multiwalled carbon nanotubes (MWCNT) are expected to be a promising adsorbent due to its excellent mechanical characteristics, nanometer size and high surface area [16].

Functionalized MWCNTs with hydroxyl group was used in the experiments. The purity of the MWCNTs was more than 95%. The OH content was about 5.58wt%, with OD less than 8nm and the length of 10–30 μm. The specific surface area was more than 500 m^2/g and the real density was about 2.1 g/cm^3.

2.2. Adsorption process

Two parameters of pressure and temperature, influencing the adsorption equilibria, were considered as the process variables. The equilibrium adsorbed amount was measured by volumetric method at the equilibrium condition. Before each experiment, pretreatment of the adsorbent was carried out in the adsorption cell by N_2 purge gas at 523 K for four hours.

According of experimental design table, three levels of temperatures and pressures were selected as the variables and the adsorption tests were carried out at the temperatures of 288.15, 298.15 and 308.15 K, and initial pressures of 4.50, 16.65 and 28.80 bar in the single batch adsorption cell for hydrogen, methane and carbon dioxide. The batch experiments were carried out in a stainless steel setup at moderate

temperatures and pressures of above atmosphere. The detailed illustration of the experimental setup is explained elsewhere [10, 11, 17].

2.3. Experimental design

This study was carried out according to a kind of experimental design called face centered central composite design method. Central composite design (CCD) is the most popular response surface method which is useful in response surface methodology, for building a quadratic model for the response variable without needing to use a complete three level factorial experiment. That is, this method is able to study the effect of the variables at different levels with fewer experiments than those of factorial design. On the other hand, it provides an alternative to attain a statistical model and optimize the adsorption conditions [18].

This design method included a total of 2^k+2k+n runs, where k is the number of factors studied (temperature and pressure, k=2), 2^k are the points from a factorial experiment, i.e. four for square experiments, 2k are the number of points carried out on the axes at a distance of $\pm\alpha$ from the center, a two variable central composite design is face centered if $\alpha=1$, and n is the number of center points. In this method, the number of center point is equal to 1 (n=1) [19].

The studied ranges of the two factors, i.e. X_1 and X_2 are listed in Table 1. It comprises the values of two parameters examined, X_1 (temperature) and X_2 (pressure), expressed in coded units -1, 0 and +l. The actual values of each parameters in succeeding experiments are to be arranged according to the coded parameters, i.e., appointing each parameter on its lower level if the corresponding coded unit is equal to -1, on the middle level if the coded unit is equal to 0, and on the upper level if the coded unit is equal to +l. For the sake of simplicity, the values of the factors are presented as coded units in Table 2.

Design Expert version 6 was applied for performing the experimental design and the data analysis. The data were analyzed with multiple regressions to fit the incomplete second order equations to all independent variables. CCD method was used to define the optimum conditions for adsorption. Initially, the analysis of variance was carried out for linear, 2FI (consist of interaction) and quadratic models. With respect to 95% confidence interval, if P-value would be lower than 0.05, the model is significant. After choosing the best regression model, analysis of variance was carried out to investigate the effect of each parameters of the model. After performing the experimental runs, the responses were determined as the amount of equilibrium adsorbed at each pressure and temperature, which they are reported in Table 3.

3. RESULTS AND DISCUSSION

3.1. Effects of factors

The influence of the operating conditions, temperature and pressure, on the equilibrium adsorption was determined experimentally and analyzed statistically. The main and interaction effects of parameters are obtained by subtracting the mean value of their positive products and their negative products. The interaction plot for hydrogen, methane and carbon dioxide adsorption versus the levels of parameters have been illustrated in Figure 1. An interaction plot is a plot of means for each level of a factor with the level of a second factor held constant and they are useful for judging the presence of interaction. Interaction is present when the response at a factor level depends upon the level(s) of other factors. Parallel lines in an interaction plot indicate no interaction. The greater the departure of the lines from the parallel state, the higher the degree of interaction.

As shown in Figure 1, temperature and pressure have negative and positive effects on the adsorption capacity of H_2, CH_4 and CO_2, respectively. It means that temperature decrease and pressure increase can cause enhancement of gas adsorption. Because of no parallel lines in interaction plot, there is an interaction effect between temperature and pressure. According to the slope of lines, pressure is more sensitive for adsorption of hydrogen, methane and carbon dioxide than temperature. In low pressure, temperature difference has no significant effect on the hydrogen adsorption. In the other words,

temperature decreasing causes to adsorption enhancement in high pressure, but in low pressure, temperature decreasing has no significant effect. The significant effect of temperature, pressure, quadratic relation and their interactions can be determined by analysis of variance.

3.2. Analysis of variance

The theory of analysis of variance (ANOVA) is well discussed by Allus et al [20]. Using the Fisher variance ratios of the parameter effect dispersion to the error dispersion, called F-test, can conclude which parameters are significant or non- significant. In this research, 95% confidence interval has been used for evaluation of the parameters signification; therefore a probability value (P-value) of 5% would be the significant level in F-tests for interpretation of the effects [21]. Analysis of variance (ANOVA) was employed in order to determine the relationship between hydrogen, methane and carbon dioxide adsorption and at least one of the two factors. In addition, by using ANOVA, it can be assessed which of the factors appear to have a greater influence on the gas adsorption. In this method various regression models can be proposed as a function of variables and their interactions, then the best model can be obtained using the residual analysis and dispersion of the responses.

3.3. Regression model

The equilibrium adsorbed amount of hydrogen, methane and carbon dioxide according to the temperature and pressure are modeled. Three types of models were selected and tested; linear model as a linear relationship of temperature and pressure, 2FI (two factor interaction) model with binary interactions of temperature and pressure, and a quadratic model which has added the second order relationship of the variables to the last model. These models are fitted on the experimental results using the linear least square method. The significance of the model is tested by F-test and the adjusted coefficient of determination (R^2_{adj}) is obtained to recognize the best fitted model. The results for hydrogen, methane and carbon dioxide adsorption are reported in Table 4, Table 5 and Table 6, respectively. In these tables, SS represents the sum of square of each coefficient in its coded unit and MSS represents the ratio of SS over DF as the mean square of that coefficient. DF is the degree of freedom of model.

As shown in Table 4, 5 and 6, according to the P-value of different models, all of the linear, two factor interaction (exception of 2FI model for hydrogen) and quadratic models are significant for hydrogen, methane and carbon dioxide. Because of the higher R^2_{adj} of quadratic model compared to the other models, it seems that quadratic models is more precise for predicting H_2, CH_4 and CO_2 adsorption. It is observed that R^2_{adj} for quadratic model of CO_2 adsorption is 1.0. It means that quadratic model can explain 100% of the total variability of the data.

The general forms of the quadratic model are presented as equations (1). In these equations, Y is the studied response, x_i and x_j are the variables considered in the study and β_0, β_i and β_{ji} are the estimated coefficients.

$$Y = \beta_0 + \sum_{1}^{k} \beta_i x_i + \sum \beta_i x_i^{\,2} + \sum_{ji} \beta_{ij} x_i x_j \qquad (1)$$

In order to show the importance of each terms of the suggested models, the coefficient on coded unit, F-value and P-value of each model parameters are summarized in Tables 7, 8 and 9.

The coefficients of each equation should be compared with the residual error of the experiments by analysis of variance to determine the signification of each term in proposed model. The F-test values and probability (P-value) values are calculated by DX6 software for each gas. In analysis of variance (ANOVA) with 95% confidence interval, those P-values with less than 5% show the signification of that parameter.

According to P-values, temperature, pressure, T-P interaction and quadratic function of pressure are significant terms in adsorption of CH_4 and CO_2. As a matter of fact, the calculated F-values of X_1, X_2, X_2^2 and X_1X_2 are much higher than X_1^2. The high value of the calculated Fi means a great influence of that factor on the experimental outcome. For adsorption

Table 1: *The factors and their levels*

Factor	Low level	High level
Temperature (X_1), K	288.15	308.15
Pressure (X_2), bar	4.50	28.80

Table 2: *Actual and coded units of the two factors*

Factor \ Coded unit	-1	0	+1
X_1	288.15	298.15	308.15
X_2	4.50	16.65	28.80

Table 3: *Experimental points of gas adsorption according to the levels defined in face centered method*

Run order	X_1	X_2	Responses		
			H_2 adsorption (mmol/g)	CH_4 adsorption (mmol/g)	CO_2 adsorption (mmol/g)
1	-1	0	0.062	2.388	15.414
2	+1	-1	0.012	0.759	4.868
3	-1	+1	0.111	3.462	21.730
4	0	0	0.054	2.130	13.142
5	+1	0	0.050	1.903	11.460
6	0	+1	0.094	2.993	18.595
7	-1	-1	0.017	1.106	6.8124
8	0	-1	0.015	0.88	5.749
9	+1	+1	0.085	2.808	16.186

Table 4: *Overall F-test on the prediction model of hydrogen adsorption*

Source of variance	DF	SS	MSS	F-value	p-value	R^2_{adj}
Linear	2	0.010	0.0052	236.48	< 0.0001	0.99
Interaction	3	0.011	0.0036	1133.98	< 0.0001	1.00
Quadratic	5	0.011	0.0021	576.81	0.0001	1.00

Table 5: *Overall F-test on the prediction model of methane adsorption*

Source of variance	DF	SS	MSS	F-value	p-value	R^2_{adj}
Linear	2	7.45	3.72	287.87	< 0.0001	0.99
Interaction	3	7.47	2.49	230.08	< 0.0001	0.99
Quadratic	5	7.52	1.50	796.60	< 0.0001	1.00

Table 6: *Overall F-test on the prediction model of carbon dioxide adsorption*

Source of variance	DF	SS	MSS	F-value	p-value	R^2_{adj}
Linear	2	276.39	138.19	151.91	< 0.0001	0.98
Interaction	3	279.63	93.21	209.93	< 0.0001	0.99
Quadratic	5	281.81	56.36	4034.76	< 0.0001	1.00

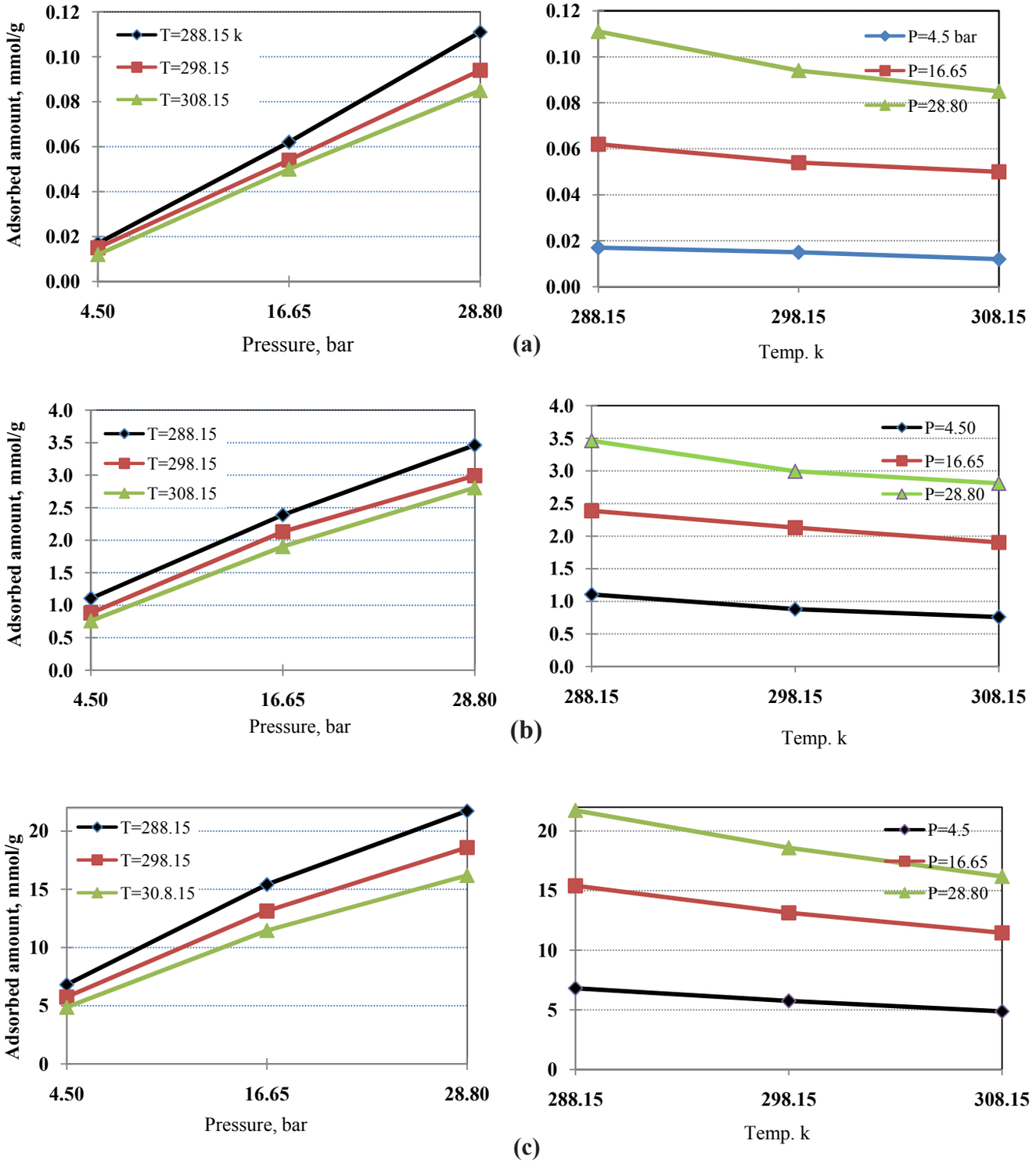

Figure 1: *Interaction plots for a) hydrogen, b) methane and c) carbon dioxide adsorption*

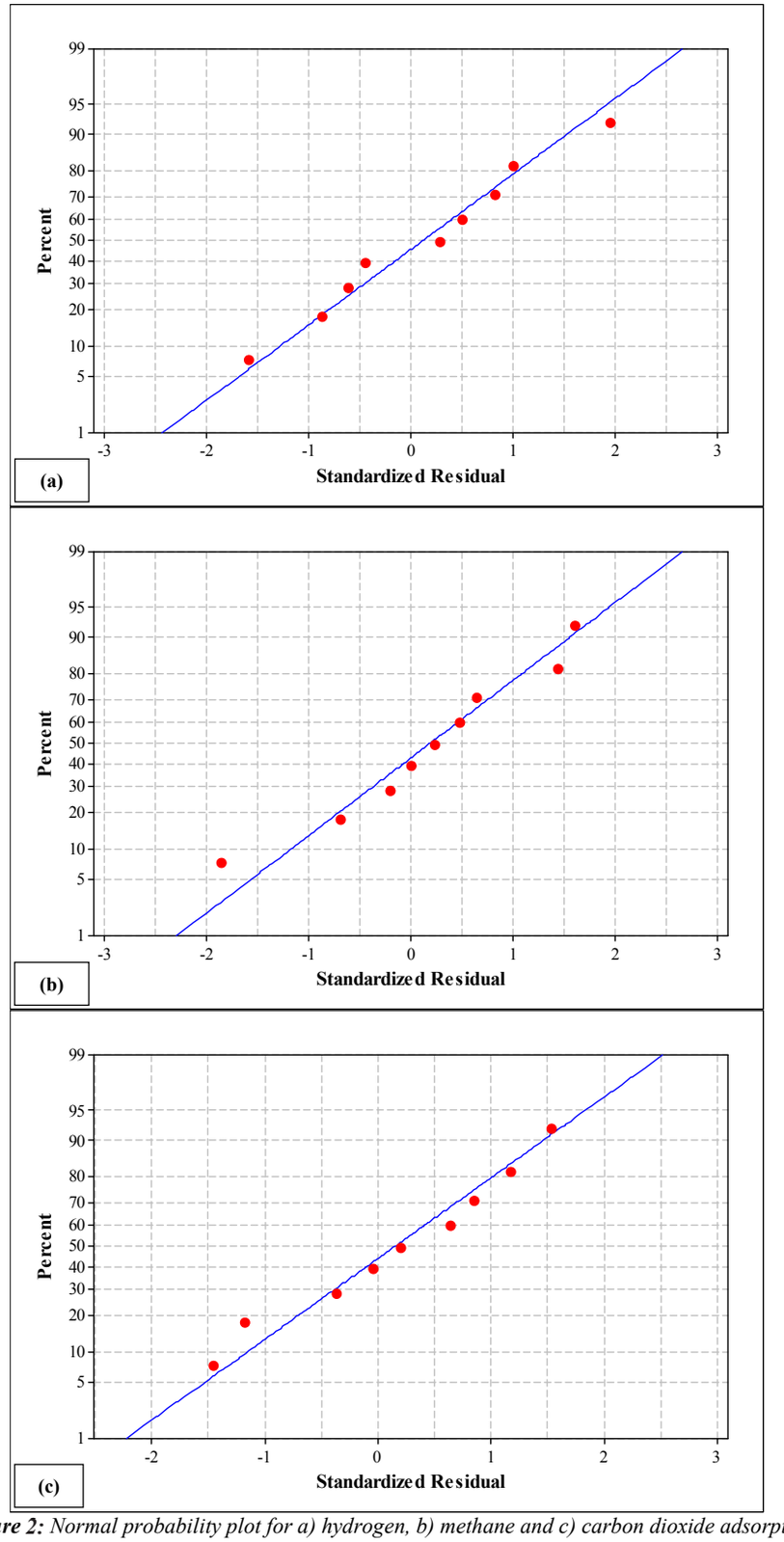

Figure 2: *Normal probability plot for a) hydrogen, b) methane and c) carbon dioxide adsorption*

Table 7: *The ANOVA of the hydrogen adsorption model*

Term	Coefficient	F-value	P-value
constant	0.054		
X_1	-0.007	85.66	0.0027
X_2	0.041	2765.23	< 0.0001
$X_1 X_2$	-0.005	31.93	0.0110
X_1^2	0.001	1.04	0.3826
X_2^2	-0.006	0.20	0.6883

Table 8: *The ANOVA of the methane adsorption model*

Term	Coefficient	F-value	P-value
constant	2.09		
X_1	-0.25	194.81	0.0008
X_2	1.09	3750.09	< 0.0001
$X_1 X_2$	-0.08	12.44	0.0387
X_1^2	0.07	5.19	0.1072
X_2^2	-0.14	20.48	0.0202

Table 9: *The ANOVA of the carbon dioxide adsorption model*

Term	Coefficient	F-value	P-value
constant	13.17		
X_1	-1.91	1563.48	< 0.0001
X_2	6.51	18222.58	< 0.0001
$X_1 X_2$	-0.90	231.81	0.0006
X_1^2	0.25	8.85	0.0589
X_2^2	-1.01	147.08	0.0012

Table 10: *Experimental points of selectivity according to the levels defined in face centered method*

Run order	X_1	X_2	Responses		
			CO_2/CH_4 selectivity	CO_2/H_2 selectivity	CH_4/H_2 selectivity
1	-1	0	6.46	249.99	38.73
2	+1	-1	6.42	404.87	63.10
3	-1	+1	6.28	195.38	31.13
4	0	0	6.17	242.45	39.29
5	+1	0	6.02	230.64	38.32
6	0	+1	6.21	196.89	31.69
7	-1	-1	6.16	403.28	65.47
8	0	-1	6.53	375.45	57.45
9	+1	+1	5.76	190.99	33.13

Table 11: *Overall F-test on the prediction model of CO_2/CH_4 selectivity*

Source of variance	DF	SS	MSS	F-value	p-value	R^2_{adj}
Linear	2	0.20	0.10	2.45	0.1669	0.45
Interaction	3	0.35	0.12	5.84	0.0434	0.78
Quadratic	5	0.38	0.076	3.32	0.1761	0.85

Table 12: *Overall F-test on the prediction model of CO_2/H_2 selectivity*

Source of variance	DF	SS	MSS	F-value	p-value	R^2_{adj}
Linear	2	60150.55	30075.27	28.25	0.0009	0.90
Interaction	3	60159.50	20053.17	15.72	0.0056	0.90
Quadratic	5	65988.12	13197.62	71.92	0.0025	1.00

Table 13: *Overall F-test on the prediction model of CH_4/H_2 selectivity*

Source of variance	DF	SS	MSS	F-value	p-value	R^2_{adj}
Linear	2	1352.21	676.10	23.67	0.0014	0.89
Interaction	3	1357.00	452.33	13.57	0.0077	0.89
Quadratic	5	1501.38	300.28	40.53	0.0059	0.99

Table 14: *Optimal conditions for maximizing CO_2/CH_4 selectivity*

Temp. (K)	Press. (bar)	CO_2/CH_4 Selecivity	Desirability
308.15	4.50	6.44	0.88

Table 15: *Optimal conditions for maximizing CO_2/H_2 selectivity*

Temp. (K)	Press. (bar)	CO_2/H_2 Selecivity	Desirability
288.15	4.50	398.23	0.97

Table 16: *Optimal conditions for maximizing CH_4/H_2 selectivity*

Temp. (K)	Press. (bar)	CH_4/H_2 Selecivity	Desirability
288.15	4.50	62.13	0.90

model of H_2, only X_1, X_2 and X_1X_2 are significant parameters. In the present study, the F-values of pressure are much higher than the other factors and it reveals a great effect of pressure on the adsorption capacity of these gases on MWCNT.

In the second try, according to the results of the ANOVA analyses presented in Tables 7, 8 and 9, the non-significant term of each model are dropped from the first regression adsorption model and the data are reanalyzed. After deleting non significant parameter, final models on coded unit for gas adsorption were achieved as equations of (2), (3) and (4). The R^2_{adj}

values for all of these models are 1.0.

$$Y_{H_2} = 0.054 - 0.007\,X_1 + 0.041\,X_2 - 0.005\,X_1X_2 \quad (2)$$

$$Y_{CH_4} = 2.09 - 0.25\,X_1 + 1.09\,X_2 - 0.14\,X_2^2 - 0.08\,X_1X_2 \quad (3)$$

$$Y_{CO_2} = 13.17 - 1.91\,X_1 + 6.51\,X_2 - 1.01\,X_2^2 - 0.90\,X_1X_2 \quad (4)$$

The normal probability plot of the standardized residuals of the final regression model is given in Figure 2. Normal probability plot indicates whether the residuals follow a normal distribution, in which case the points will follow a straight line.

The normal probability plot for the standardized residuals of the second correlation, as shown in Figure 2, indicates that these models has a smaller deviation from the straight line. Therefore, the residuals of the second regression model come from a nearly normal distribution. In regression as a statistical method, it is assumed that residuals are normally distributed. Since the residuals of the second regression model have an approximately normal distribution, it is concluded that the major underlying assumption of regression, in fact, is true for the second correlation.

3.4. Nanotubes selectivity

In addition to the adsorbed capacity, the CO_2/CH_4, CO_2/H_2 and CH_4/H_2 selectivity of nanotube that is an important response in separation processes by adsorption technology, was investigated. Selectivity of the nanotube was calculated by the ratio of equilibrium adsorption capacity of gases, for example CO_2/CH_4 selectivity was calculated by the ratio of equilibrium adsorption of CO_2 over CH_4. The significance of the model was tested by F-test and the adjusted coefficient of determination (R^2_{adj}) was obtained to recognize the best fitted model. CO_2/CH_4, CO_2/H_2 and CH_4/H_2 selectivities in studied rang of temperatures and pressures are presented in table 10. The results for CO_2/CH_4, CO_2/H_2 and CH_4/H_2 selectivity are reported in Table 11, Table 12 and Table 13, respectively.

As shown in Table 11, 12 and 13, according to the P-value and R^2_{adj} of different models, quadratic model is significant for CO_2/H_2 and CH_4/H_2 selectivity and 2FI model is significant for CO_2/CH_4 selectivity. Significant model for CO2/CH_4, CO_2/H_2 and CH_4/H_2 selectivity in term of coded unit after dropping non significant parameters, are shown as equations of (5), (6) and (7).

$$Y_{CO_2/CH_4\ selectivity} = 6.22 - 0.12\,X_1 - 0.14\,X_2 - 0.19\,X_1X_2 \quad (5)$$

$$Y_{CO_2/H_2\ selectivity} = 241.03 - 3.69\,X_1 - 100.06\,X_2 + 53.45\,X_2^2 \quad (6)$$

$$Y_{CH_4/H_2\ selectivity} = 38.78 - 0.13\,X_1 - 15.01\,X_2 + 8.22\,X_2^2 \quad (7)$$

According to the coefficients of the models, quadratic effect of pressure exhibits the significant effect on CO_2/H_2 and CH_4/H_2 selectivity.

3.5. Optimization

There are two main different strategies for optimization; simplex optimization and response surface methodology. An exact optimum can only be determined by response surface methodology, while the Simplex method will encircle the optimum, therefore response surfaces are used to perform the optimal conditions. In addition, it is a good way to graphically illustrate the relation between different experimental variables and responses [22].

Two parameters of temperature and pressure were optimized in order to quantitatively determine the maximum CO_2/CH_4, CO_2/H_2 and CH_4/H_2 selectivity. The optimal point was found with its desirability and the results are shown in Table 14, 15 and 16. The desirability provides an overall measure for the goodness of the specific setting. A large value indicates a desirable set of values for the various responses; a low value indicates an undesirable set of values. Desirability is an objective function that ranges from zero outside of the limits to one at the goal. The numerical optimization finds a point that maximizes the desirability function [23]. It is concluded that the optimal point are achieved at the pressure of 4.50 bar and temperature of 308.15 K for CO_2/CH_4 selectivity and 288.15 K for CO_2/H_2 and CH_4/H_2 selectivity.

4. CONCLUSIONS

In this work, equilibrium adsorption of H_2, CH_4 and CO_2 by MWCNT-OH was studied by design of experiments and statistical analysis. Two parameters including temperature and pressure were considered as the main factors affecting the performance of the adsorption. Effect of these parameters, interaction and quadratic functions were studied by the face centered central composite design of experiments. Analysis of variance and regression method suggest that gas adsorption is considerably enhanced by pressure increasing. On the other hand, the adsorption is decreased by temperature increasing. In addition to gas adsorption, the best models for CO_2/CH_4, CO_2/H_2 and CH_4/H_2 selectivity and finally the optimal condition to maximize the selectivities were achieved. It is concluded that for effective separation of CO_2 from CH_4 by CMWNT-OH it is better to work at 308.15 K and pressure of 4.50 bar, where a selectivity of 6.44 for CO_2/CH_4 is determined, for more efficient separation of CO_2 from H_2 working at 288.15 K and 4.50 bar is preferred with a selectivity of 398.23 and for separation of CH_4 from H_2 stream it is proposed to proceed at 288.15 K and 4.50 bar, in which the obtained selectivity would be 62.13. As a result, MWCNT-OH could be a very good candidate for separation of CO_2 and CH_4 impurities from hydrogen because of very high selectivities resulted from experiments and optimization. In addition it should be noted that separation of CO_2 from CH_4 by this adsorbent could be possible although with much lower selectivity.

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