Process Optimization of Carbon Dioxide Adsorption using Nitrogen-Functionalized Graphene Oxide via Response Surface Methodology Approach

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This paper presents a response surface methodology approach in the optimization of the carbon dioxide temperature-programmed adsorption process using a new material referred as nitrogen-functionalized graphene oxide. This material was synthesized by loading nitrogen groups to graphene oxide using aqueous ammonia in supercritical condition. Later on, it was utilized as a sorbent for carbon dioxide adsorption. This process was optimized by implementing a response surface methodology coupled with a Box-Behnken design for the effects of three factors: adsorption temperature, carbon dioxide flow rate, and the amount of adsorbent. In analyzing the response surface, a model equation was generated based on the experimental data by regression analysis. This model equation was then utilized to predict optimum values of response. Furthermore, response optimizer was also conducted in identifying factor combination settings that jointly optimize the best response.

INTRODUCTION

The accumulation of carbon dioxide (CO_2) in the atmosphere is considered to be a major environmental hazard. CO_2 concentrations in the atmosphere has increased by 40 % since pre-industrial times (IEA, 2015). In this regard, studies were conducted to develop a stable, safe, and environmentally acceptable method for CO_2 capture and storage emissions. Among numerous technologies available for CO_2 capture, adsorption using solid adsorbent were preferred to address

existing drawbacks of other technologies. The advantages of this technology are its adsorbents were relatively thermally stable, corrosion resistant, with high loading capacities, and with tunable surfaces (Sayari et al. 2011, Lu et al. 2014). This method is continuously developed by evaluating other possible solid adsorbents to increase CO_2 adsorption capacity such as incorporating amine-based functional groups to mimic a solid amine-based sorbent (Serna- Guerrero et al. 2010). Meanwhile, aqueous ammonia (NH_3aq) was one of the promising liquid solvents that were previously studied using absorption process (Diao et al. 2004, Jilvero et al. 2014). The use of this in CO_2 capture was not yet commercialized due to problems such as volatilization, thermally unstable, and causes corrosion (Zhao et al. 2012). In this regard, the use of NH_3 aq was further explored in adsorption process as a source of N-group and was loaded into a graphene oxide (GO). The new material referred as nitrogen-functionalized graphene oxide (N-FGO) were characterized and evaluated for CO_2 adsorption. Details of functionalization and characterization results were reported in another paper (Baldovino et al. 2016). It was observed that this material is thermally stable, does not volatilize and is corrosion resistant. The main objective of this study is to optimize the operating parameters involved in CO_2 adsorption processes such as temperature (^0C), CO_2 flow rate (ml/min), and the amount of adsorbent (mg). Response surface methodology (RSM) coupled with Box-Behnken design (BBD) was utilized.

METHODS

Nitrogen–Functionalization of Graphene Oxide

As-prepared GO (a detailed process discussed in Baldovino et al. 2016) was functionalized with N-groups via supercritical (SC) conditions. GO was combined with NH_3 aq in a batch reactor and was subjected to supercritical conditions (300°C and 40 MPa as the critical temperature and pressure of NH_3, respectively) inside a furnace. The detailed functionalization method was reported elsewhere (Baldovino et al. 2016). Thereafter, it was filtered and then dried in an oven at 60°C for 24 h. The resulting material referred to as N-FGO were then tested in CO_2 adsorption process as a sorbent.

Carbon Dioxide Adsorption Measurements

The CO_2 temperature-programmed adsorption (TPA) performance of the N-FGO was evaluated in a modified setup of TG/DTA 6300 at atmospheric pressure. A certain amount of an adsorbent was placed in a small aluminum pan and was loaded inside the TGA. First, it was heated at 120°C for 30 min to remove moisture content. The analysis adsorption temperature was then set with a continuous flow of N_2 gas until the system was stable. N_2 gas was then turned OFF and pure CO_2 gas was flowed into the system for 180 min to achieve complete saturation. The weight increase after the adsorption process was referred to as the adsorption capacity of the adsorbent.

Design of Experiment and Statistical Analysis

The CO_2 TPA process using N-FGO were optimized and evaluated using RSM-BBD. Statistical software, MINITAB 14 and JMP, were used to generate experimental designs, statistical analyses, and regression models. A quadratic polynomial equation was used to predict the dependent variables (responses) as a function of independent variables (factors) and their interactions (see Equation 1).

$$y = b_0 + b_1x_1 + b_2x_2 + b_3x_3$$
$$+ b_{11}x_1^2 + b_{22}x_2^2 + b_{33}x_3^2 \qquad (1)$$
$$+ b_{12}x_1x_2 + b_{13}x_1x_3 + b_{23}x_2x_3$$

To interpret the regression coefficients for curvilinear relationships and interaction terms, a response surface regression was used to develop the model equation. Analysis of variance (ANOVA) was applied to determine the goodness of fit of the model, main effects and interactions between factors and response(s). The goodness of fit can be evaluated through the coefficients of determination, R^2, and R^2adj. This is used to summarize the difference between observed values and values expected under the model in question. The higher the value of R^2 and R^2adj indicates that the model explains all the variability of the response data around its mean (Körbahti et al. 2008).

Thereafter, insignificant factors were eliminated depending on P-value. P-value lower than 0.05 indicates that the factor is statistically significant based on 95% confidence interval (Choi et al. 2014). Lastly, the final model based on Equation 1 was obtained.

RESULTS AND DISCUSSIONS

Statistical Analysis on Temperature Programmed CO_2 Adsorption

An experimental design was prepared based on factors and levels listed in **Table 1**. Factors include: temperature (x_1, ^{0}C), CO_2 flowrate (x_2, ml/min), and amount of adsorbent (x_3, mg). The levels of each factor were designated by coded units using −1, 0 and 1 that pertains for low, middle and high values, respectively.

Table 1. Generation of 3-factor, 3-level response surface design

Factors	Levels		
	−1	0	1
x_1: Temperature (^{0}C)	40	80	120
x_2: CO_2 flowrate (mL/min)	100	200	300
x_3: Amount of adsorbent (mg)	4	6	8

These variables and their respective values were chosen based on results of preliminary runs conducted and from the existing limitations of the set-up utilized in the CO_2 TPA. In detail, lower and upper values of adsorption temperature were chosen as 40°C and 120°C, since no or less adsorption will occur at temperatures lower than 40°C and greater than 120°C. Likewise, low adsorption occurs at values lower than 100 ml/min and greater than 300 ml/min of CO_2 flowing. Also, less adsorption occurred at values lower than 4 mg of adsorbent. Moreover, the sample holder can only accommodate around 8mg of the sample.

Using RSM-BBD, an experimental design layout with 15 runs was generated (see **Table 2**). The experimental runs were in a randomized order to minimize the effects

Table 2. Experimental design layout and experimental results of response

Run No.	Coded variables			Actual variables			Response Y
	x_1	x_2	x_3	x_1	x_2	x_3	
1	0	1	-1	80	300	4	0.002
2	1	1	0	120	300	6	0.0009
3	-1	0	1	40	200	8	0.00272
4	0	-1	1	80	300	8	0.006
5	0	0	0	80	200	6	0.00084
6	-1	1	0	40	300	6	0.00126
7	-1	0	-1	40	200	4	0.0004
8	0	-1	1	80	100	8	0.00688
9	-1	-1	0	40	100	6	0.00186
10	0	-1	-1	80	100	4	0.00296
11	1	0	-1	120	200	4	0.00024
12	0	0	0	80	200	6	0.00072
13	0	0	0	80	200	6	0.00114
14	1	0	1	120	200	8	0.00288
15	1	-1	0	120	100	6	0.00084

Table 3. Estimated regression coefficients and ANOVA for CO_2 TPA

Source**	Sum of squares	Degrees of freedom	Mean square	F-value	p-value	Result
Model	5.27e-6	9	5.85e-7	17.8782	0.042	significant
x_1	2.4e-7	1	2.4e-7	0.7266	0.433	not significant
x_2	7.1e-7	1	7.1e-7	2.1612	0.201	not significant
x_3	2.07e-5	1	2.07e-5	63.2953	0.001	significant
$x_1 * x_2$	1.1e-7	1	1.1e-7	0.3324	0.589	not significant
$x_1 * x_3$	2.56e-8	1	2.56e-8	0.0781	0.791	not significant
$x_2 * x_3$	1.6e-9	1	1.6e-9	0.0049	0.947	not significant
$x_1 * x_1$	6.17e-6	1	6.17e-6	18.8273	0.007	significant
$x_2 * x_2$	9.54e-6	1	9.54e-6	29.1226	0.003	significant
$x_3 * x_3$	1.41e-5	1	1.41e-5	42.9645	0.001	significant
Residual	1.6381e-6	5	3.27e-7	-	-	
Lack of fit	1.5445e-6	3	5.13e-7	11.0007	0.0845	not significant
Pure error	9.36e-8	2	4.68e-8	-	-	
R^2 (0.9700) and R^2 adjusted (0.9160)						

** x_1: temperature, x_2: CO_2 flow rate, x_3: amount of adsorbent

of the uncontrolled factors. After CO_2 TPA, the response (Y) amount of CO_2 adsorbed (mmol CO_2) were recorded in the same table. From the results, the range of response was observed from 0.00024 to 0.00688 mmol CO_2.

An analysis of variance (ANOVA) was conducted to analyze the fitness of model and the interactions between the variables and response (See **Table 3**). The goodness of fit of the polynomial model was determined by the high value of the coefficient of determination, R^2 (0.97) and R^2 adjusted (0.9160). Significant factors along with the constant were identified as the following: x_3, x_1^2, x_2^2, and x_3^2. The final model equation using coded units after eliminating the insignificant factors is
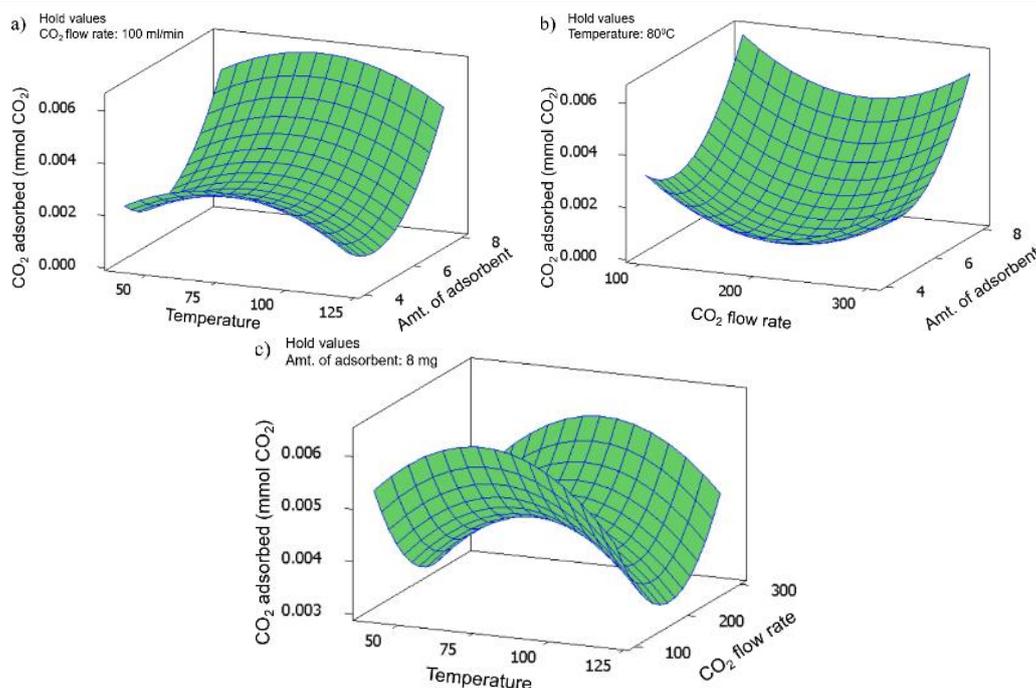
Fig. 1: Wireframe surface plots for (a) temperature and amt. of adsorbent, (b) CO_2 flow rate and amt. of adsorbent, and (c) temperature and CO_2 flow rate.

reported in Eq. 2.

$$y = 0.000900 + 0.00161x_3 \\ -0.001292x_1^2 + 0.0016808x_2^2 \quad (2) \\ +0.001953x_3^2$$

This model equation based form coded units can predict the response by inputting different values for each factor as well as determining the optimal response. Thus, optimized parameters and response are reported in **Table 4**.

Table 4. Optimized Conditions for CO_2 TPA

Parameter	Values
x_1: Temperature	80^0C
x_2: CO_2 Flowrate	100 mL/min
x_3: Amount of adsorbent	8 mg
Y (predicted value)	0.0063 mmol CO_2

A comparison of 3D wireframe surface plots was prepared to further visualize the relationship between factors. Predictor factors are represented by the x- and y-axis and the response are displayed on the z-axis. One factor is fixed as two variables are investigated as shown in the plots in **Figure 1**.

Analysis of The Optimum CO_2 TPA Conditions

The optimized response is equal to 0.0063 mmol CO_2 when factors are set to 80^0C, 100 ml/min, and 8mg of adsorbent. An optimum temperature of 80^0C is relatively higher than the usual temperature of 25^0C in other CO_2 adsorption studies utilizing other sorbents. This will be an advantage if applied to actual post-combustion CO_2 capture by the reduction of energy required to cool down the gases before adsorption.

By evaluating the kinetics of the TPA process, CO_2 adsorption mechanism using N-FGO was found to follow a combination of physical (physisorption) and chemical

(chemisorption) interaction between the N-FGO and the CO_2 (Baldovino, 2017, De La Salle University, Ph. D. Thesis). At low temperature, adsorption followed physisorption. When the temperature was increased, most of the interactions found in the CO_2 adsorption were governed by chemisorption. At 80^0C is just appropriate to allow both physisorption and chemisorption between the N-FGO and CO_2. On the other hand, the optimum value of flowrate is 100 ml/min. If the values for flow rate were changed in the response optimizer to 200 or 300 ml/min, response values were lower. This is due to the system inside the TGA set-up used in the adsorption was continuous. When gases enter the system, it will also go out of the vent continuously. Therefore, the faster the flow rate the faster it will go out of the system leaving less time to react with the sorbent. Meanwhile, 8 mg of adsorbent is necessary to attain an optimum response. When the amount was set to lower than this, the response was also lower. The higher the surface area exposed the higher the adsorbed CO_2. The sample sorbent holder is also important. The holder is made of a circular pan with a size just enough to contain around 7 mg of sample. When 8 mg of samples was used, it exceeded the capacity of the holder, therefore, creating a mountain or pile of samples on top. Thus, providing more surface area to react with the CO_2. Unlike when the amount of sorbent is lower, it is just enough to fill in the holder fixing the surface area available for reacting.

Reproducibility Runs Prepared Under Optional Conditions

To evaluate the reproducibility and accuracy of the model and the optimal conditions predicted, three confirmations runs were conducted. The average values of these repeated runs were reported and compared with the predicted value in **Table 5**. As can be seen, the experimental results were not significantly different with the predicted value as indicated by the deviation error. The close agreement between the experimental and the predicted value suggest that the developed model can correlate the CO_2 TPA factors/parameters to CO_2 adsorption with a high degree of accuracy.

Table 5. Predicted a experimental values of the studied response obtained at optimum condition

Response	Experimental results*	Predicted value	Error (%)
CO_2 adsorption capacity (mmol CO_2)	0.0062	0.0063	1.59%

* Represents the average values of the repeated experiments

CONCLUSION

The temperature-programmed CO_2 adsorption using N-FGO was optimized by response surface methodology with Box-Behnken design (RSM-BBD). Optimal values of the response (amount of CO_2

adsorbed: 0.0063 mmol CO_2/8 mg adsorbent) and factors (temperature: 80^{0}C, CO_2 flow rate: 100 ml/min, and the amount of adsorbent: 8 mg) were also determined based on the RSM-BBD. A model equation was generated to predict the amount of the CO_2 adsorbed at any values of temperature, CO_2 flow rate, and the amount of adsorbent used. This model will be useful as a basis for future similar studies to predict values of factors and responses to further improve the process.

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