

Statistical Modeling and Optimization of Amination Conditions of Activated Carbon for Carbon Dioxide Adsorption Using Response Surface Methodology

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Abstract. The surface modification of activated carbon with gaseous ammonia for obtaining an efficient carbon dioxide (CO₂) adsorbent was optimized using the response surface methodology. The variables chosen were amination temperature, amination time, and the use of pre-heat treated (HTA) or pre-oxidized (OXA) sorbent as the starting material, while the responses were CO₂ adsorption and desorption capacity. Among process parameters studied, amination temperature was found to have the most significant effect on both the studied responses. Quadratic models developed for the two responses studied (dependent variables) indicated the optimum conditions could be obtained by using OXA sorbent with amination temperature of 425 °C and amination time of 2.1 h. The activated carbon modified at optimum condition showed CO₂ adsorption capacity of 26.1 mg/g and CO₂ desorption capacity of 94.9%. The experimental values of the responses at the optimum condition were found to agree satisfactorily with the amounts predicted by the models.

Keywords: Activated carbon, Ammonia modification, Carbon dioxide adsorption, Response surface methodology, Optimization

1. Introduction

Carbon dioxide (CO₂) is one of the most important greenhouse gases, and it is primarily released during the combustion of fossil fuels (coal, oil, and natural gas). The growing environmental concern over global warming and climate change has prompted a global research effort to stabilize the atmospheric concentration of CO₂ and mitigate the unfettered release of greenhouse gases into the atmosphere [1]. The removal of CO₂ with solid adsorbents may be a more attractive approach than conventional liquid absorbents because it could reduce the cost associated with the capture step. However, the success of this approach is dependent on the development of an easily regenerated and durable adsorbent with high CO₂ selectivity and adsorption capacities [2]. One of the most widely used adsorbents for CO₂ capture from flue gas streams is activated carbon.

Introducing basic nitrogen functionalities into the carbon surface through reactions with nitrogen-containing reagents (e.g., ammonia) can increase the capacity of activated carbon to adsorb CO₂ [3]. However, the graphitic surface of carbon does not demonstrate a high reactivity toward ammonia. Therefore, carbon is usually oxidized prior to introducing N-containing functionalities to the carbon surface [4]. In the case of high-temperature adsorption, although the role of surface chemistry and the presence of basic nitrogen functionalities is more considerable [5], only the optimization of textural properties is well reached in literature. Although the effect of surface chemistry modification on CO₂ adsorption performance depends on the modification conditions, as far as we know, no study has been done to optimize these modification conditions.

Accordingly, in the present study, RSM based on central composite design (CCD) was used to design experiments, build models and determine the optimum modification conditions for desirable responses. The main objective of this work was to investigate the effect of modification parameters (amination temperature,

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amination time, and type of starting material) on the CO₂ adsorption/desorption performance of modified sorbents so as to optimize the operating conditions of ammonia treatment.

2. Materials and Methods

2.1. Activated carbon sample

Commercial palm-shell-based granular activated carbon (GAC) was used as a starting material for the preparation of a CO₂ adsorbent. The precursor was ground and passed through a US mesh size 20-35 sieve (850-500 μm) prior to all further treatments. To eliminate fines, the GAC was then thoroughly washed with distilled deionized water (DDW), dried at 105 °C for 24 h to remove moisture, and stored in a desiccator under vacuum.

2.2. Ammonia modification

The ammonia modification of HTA was achieved by placing approximately 1 g of activated carbon in a tubular quartz reactor under a 75 cm³ min⁻¹ flow of nitrogen. The temperature of the reactor was increased at a rate of 10 °C min⁻¹ until it reached a final modification temperature (selected temperatures from 200 to 1000 °C). The feed gas (nitrogen) was then changed to reactive gas (pure ammonia) at the same flow rate. During this treatment, the samples were maintained at the final temperature for a period of time (between 1 and 3 h) and then cooled down to 100 °C at the same cooling rate (10 °C min⁻¹). Finally, the flow was changed back to N₂ until room temperature was reached.

For the modification of OXA samples, approximately 1 g of sample was placed into a quartz reactor. Air was introduced, and the reactor temperature was heated (10 °C min⁻¹) to 400 °C. This temperature was selected for air oxidation because it was reported to be the optimum temperature at which to add surface oxygen groups. The sample was held at this temperature for 2.5 h and then cooled down to room temperature before the gas was switched to pure ammonia. Both the air and NH₃ flow rates were set to 75 cm³ min⁻¹. Next, the sample was heated in an ammonia atmosphere with a heating rate of 10 °C min⁻¹ until the desired temperature was reached. The ammonia treatment was then performed with the same reaction conditions described above.

2.3. Experimental design and method of analysis

In the present work, the effects of three independent variables, including two numerical variables (i.e., amination temperature between 200 and 1000 °C (X_1) and amination times between 1 and 3 h (X_2), both at five levels, and one categorical variable (i.e., the use of HTA or OXA as the starting material (X_3)) were investigated using central composite design. These variables, along with their respective regions of interest, were chosen based on the literature and preliminary studies [6]. Table 1 presents the range and levels of the independent numerical variables in terms of actual and coded values.

Table 1. Independent numerical variables and their levels (actual and coded)

Independent numerical variables	Symbol	Coded variable levels				
		-1	-0.5	0	+0.5	+1
Amination temperature, (°C)	X_1	200	400	600	800	1000
Amination time, (h)	X_2	1	1.5	2	2.5	3

The CO₂ sorption capacity (Y_S) and desorption capacity (Y_D) of the resulting adsorbents were taken as the two responses of the designed experiments. A quadratic polynomial equation was developed to predict the dependent variables (chosen responses) as a function of independent variables (factors) and their interactions. An analysis of variance (ANOVA) was applied to identify the interactions between the amination variables and the responses.

2.4. CO₂ adsorption/desorption measurements

In a typical adsorption/desorption test, approximately 10 mg of the adsorbent was placed in a small pan and heated to 105 °C at a heating rate of 2 °C min⁻¹ under a flow of pure N₂ (75cm³min⁻¹). The sample was held isothermally (30 min) until its weight became stable. The gas was then switched to pure CO₂ at the same

flow rate. The sample was held isothermally at 105 °C under a flow of pure CO₂ for 90 min to achieve complete saturation. This temperature was selected because it is the expected temperature in a power plant flue gas desulfurization unit [5]. The weight increase during this stage was taken as the CO₂ capture capacity of the sample at 105 °C. After adsorption, the gas was switched back to N₂ at the same flow rate while the temperature was maintained at 105°C. This was done to study the desorption capacity of the adsorbents. For all of the samples, a desorption time of 30 min was selected because this is the time necessary to fully desorb CO₂ from untreated carbon.

3. Results and Discussion

3.1. Evaluation of CO₂ adsorption and desorption capacity

The best way to express the effect of amination parameters on CO₂ adsorption/desorption within the experimental range is to generate response surface plots of the equation. The linear, quadratic, and cross terms in the second-order polynomial model were used to generate a three-dimensional (3D) response surface graph and a two-dimensional contour plot. Based on the ANOVA results, the amination time (X_2), type of starting material (X_3), X_1^2 and X_2^2 were found to have significant effects, but the amination temperature (X_1) had the largest effect on both the CO₂ adsorption and desorption capacities. Furthermore, among the interaction terms, X_1X_2 and X_1X_3 were found to significantly affect the studied responses, whereas the effect of interaction between X_2 and X_3 (X_2X_3) was less pronounced (not significant). The predicted values versus experimental values for CO₂ adsorption and desorption capacity are presented in Fig. 1 (a) and (b), respectively. Experimental values represent the measured response data for a particular run, and the predicted values are generated by the models. As can be observed, the predicted values were quite close to the actual values (all points are close to the diagonal line), indicating that the regression model equation provides a sufficiently accurate description of the experimental data.

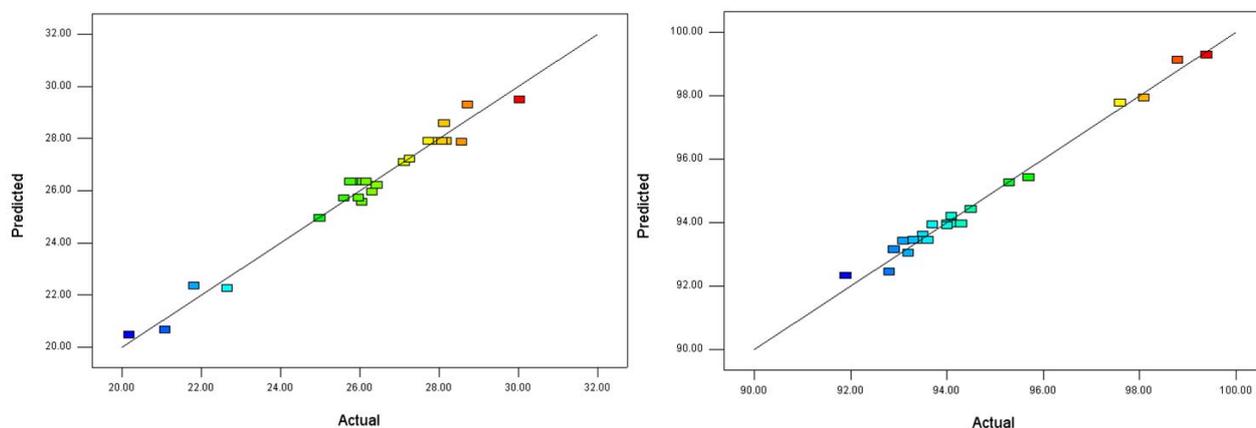


Fig. 1: Design-Expert-generated plot of predicted vs. actual values for (a) CO₂ adsorption capacity and (b) CO₂ desorption capacity.

3.2. Effect of amination variables on the CO₂ adsorption capacity

Three-dimensional (3D) response surface plots of the predictive quadratic model for the CO₂ adsorption capacity of pre-heat-treated and pre-oxidized carbon are presented in Fig. 2(a) and (b), respectively. For both types of adsorbents, CO₂ capture capacity increases as the temperature and time of the ammonia treatment increases. The synergistic effect of X_1 and X_2 factors on the Y_s response may be related to the formation of more N-containing functionalities, particularly in the form of pyrrole and pyridinic-like functionalities, which appear during high-temperature (>600 °C) amination (suitable surface chemistry) [4]. In addition, a partial gasification of the adsorbents with free radicals that were generated during the decomposition of ammonia would lead to pore enlargement, which may contribute to the enhancement of CO₂ uptake (favorable textural properties) [3]. This is in accordance with our previous findings, in which the surface chemistry and porous texture of the modified sorbent became more favorable as the amination temperature increased [5]. As can be seen in Fig. 2, in comparison with the pre-heat-treated aminated samples, the pre-oxidized carbon displayed an enhanced ability to adsorb CO₂. The greatest CO₂ adsorption capacity, 30.04

mg/g, was obtained for the pre-oxidized sample that had been modified with ammonia at 800 °C for 2 h. The increased CO₂ capture capacity observed for pre-oxidized sorbents indicates that the presence of oxygen functionalities on the carbon surface prior to ammonia treatment plays an important role in improving the CO₂ capture performance of the modified samples.

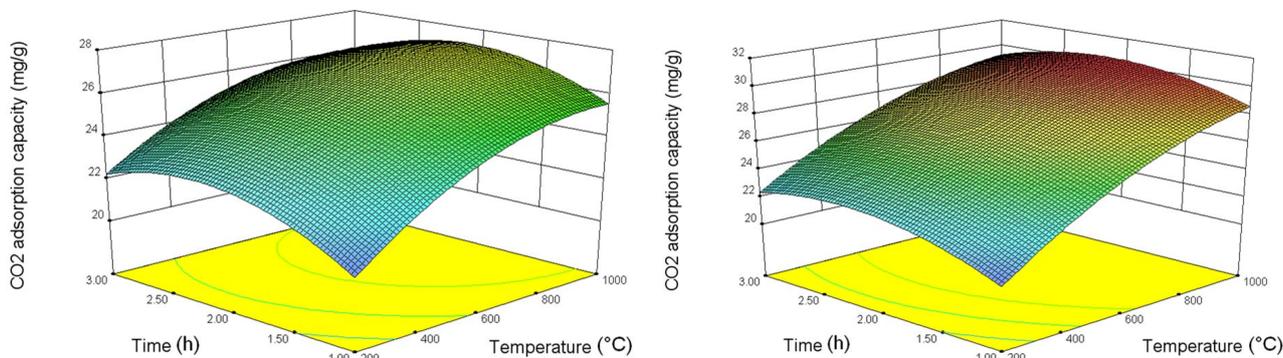


Fig. 2: Design-Expert-generated plot; response surface plot of CO₂ adsorption capacity for (a) pre-heat treated, and (b) pre-oxidized sorbent.

3.3. Effect of amination variables on the CO₂ desorption capacity

Fig. 3(a) and (b) represent the 3D response surfaces that were constructed to show the variables' effectiveness on the CO₂ desorption capacity of the modified sorbents. A decrease in desorption capacity with an increase in amination temperature and duration can be observed for both types of adsorbents. One possible reason for this observation is that for high temperature adsorption (e.g., over 100 °C), CO₂ uptake is mainly controlled by chemical adsorption [7]. In samples with favorable surface chemistries, the stronger interactions between acidic, gaseous CO₂ and the incorporated basic N-functionalities lead to the formation of stronger chemical bonds that hinder regeneration. Accordingly, the sample with the highest CO₂ adsorption capacity demonstrated the lowest desorption capacity (91.9%). In contrast, as can be seen in Fig. 3, the sample with the lowest capture capacity had the highest desorption capacity (99.4%), which may be the result of either weak chemical interactions between the CO₂ and N-functionalities or its poor textural properties compared to the other sorbents. The aforementioned conclusion was based on the chemical and textural characterization results reported from our group [5].

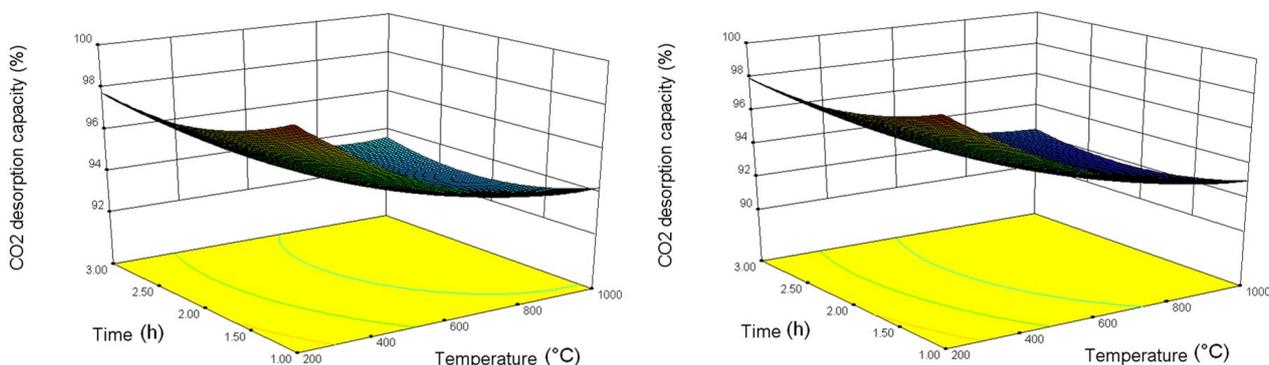


Fig. 3: Design-Expert-generated response surface plot of CO₂ desorption capacity for (a) pre-heat-treated and (b) pre-oxidized sorbent.

3.4. Investigation of the optimum amination conditions

In the production of efficient CO₂ adsorbents, relatively high capture capacities are necessary for production to be economically feasible. For practical applications, the modified sorbents should not only possess high adsorption capacities but also show high desorption capacities for economical viability. However, the CO₂ adsorption (Y_s) and desorption (Y_d) capacities are compensatory (i.e., when Y_s increases,

Y_d decreases and vice versa.) Thus, it is difficult to find a balance between high adsorption and desorption capacities. Multiple response optimizations could be generated from the contour plots of the second order model for each response in the experimental ranges of each factor (Fig. 4(a) and (b)). To identify the optimum conditions, the targeted criteria were set as maximum values for the responses (CO₂ adsorption and desorption capacity), whereas the values of the numerical variables (amination temperature and amination time) were set in the ranges studied for both HTA and OXA adsorbents. The amination conditions that showed the highest desirability were experimentally verified. The optimal point indicated by numerical optimization corresponds to a pre-oxidized sorbent that has been aminated at 425 °C for 2.1 h. Fig. 4(a) and (b) shows the contour plots for predicting the maximum CO₂ adsorption and desorption capacities, respectively, under the determined optimum conditions. It was predicted that maximum CO₂ adsorption and desorption capacities of 26.1 mg/g and 94.9 %, respectively, could be obtained for the activated carbon adsorbent. From the aforementioned optimization results, the application of post-oxidation ammonia treatment (preparation method) at 425 °C for 2.12 h (experimental conditions) was found to produce a high adsorption/desorption capacity activated carbon for carbon dioxide adsorption.

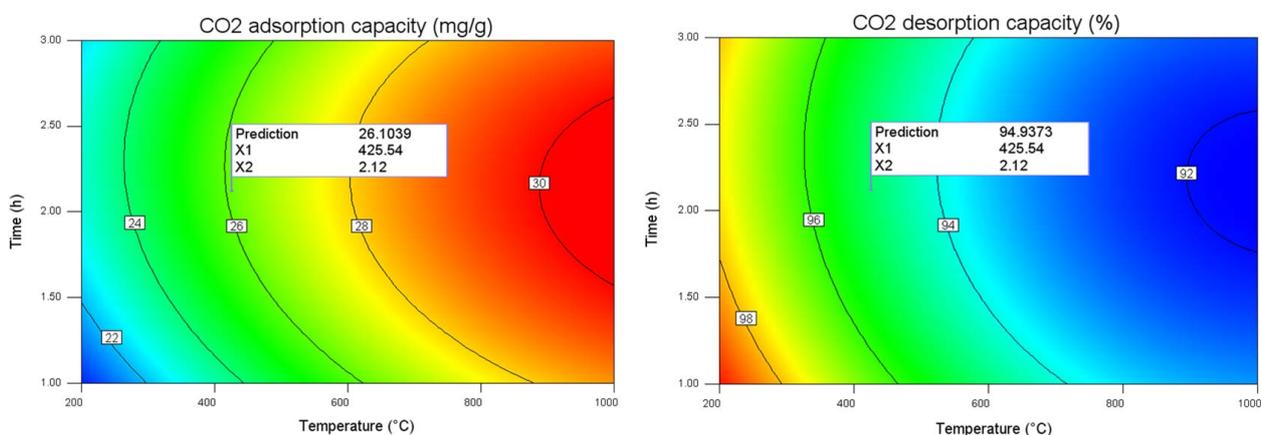


Fig. 4: Design-Expert-generated contour plots of (a) CO₂ adsorption capacity and (b) CO₂ desorption capacity as a function of amination temperature and time for pre-oxidized sorbents.

4. Conclusion

The objective of this paper was to optimize the amination conditions of activated carbon adsorbents in an effort to maximize their CO₂ adsorption/desorption capacities. The effects of amination temperature, amination time, and the type of starting materials (variables) on the CO₂ adsorption/desorption capacities of modified sorbents (responses) were investigated using a central composite design. Among the process parameters studied, the temperature of ammonia treatment was found to have the most significant positive and negative influence on the CO₂ adsorption and desorption capacity, respectively. The use of a pre-oxidized sorbent as a starting material and amination at 425 °C for 2.1 h were found to be the optimum conditions for obtaining an efficient carbon dioxide adsorbent. This material exhibited CO₂ adsorption and desorption capacity values of 26.1 mg/g and 94.9%, respectively.

5. References

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