Experimental Modeling and Optimization of CO₂ Absorption into Piperazine Solutions Using RSM-CCD Methodology

Hassan Pashaei, Ahad Ghaemi,* Masoud Nasiri, and Bita Karami

ABSTRACT: The present work evaluates and optimizes CO₂ absorption in a bubble column for the Pz-H₂O−CO₂ system. We analyzed the impact of the different operating conditions on the hydrodynamic and mass-transfer performance. For the optimization of the process, variable conditions were used in the multivariate statistical method of response surface methodology. The central composite design is used to characterize the operating condition to fit the models by the least-squares method. The experimental data were fitted to quadratic equations using multiple regressions and analyzed using analysis of variance (ANOVA). An approved experiment was carried out to analyze the correctness of the optimization method, and a maximum CO₂ removal efficiency of 97.9%, an absorption rate of 3.12 g/min, an NCO₂ of 0.0164 mol/m²·s, and a CO₂ loading of 0.258 mol/mol were obtained under the optimized conditions. Our results suggest that Pz concentration, solution flow rate, CO₂ flow rate, and speed of stirrer were obtained to be 0.162 M, 0.502 l/h, 2.199 l/min, and 68.89 rpm, respectively, based on the optimal conditions. The p-value for all dependent variables was less than 0.05, and that points that all three models were remarkable. In addition, the experiment values acquired for the CO₂ capture were found to agree satisfactorily with the model values (R² = 0.944−0.999).

1. INTRODUCTION

Control and mitigation of the emission of carbon dioxide, the most significant contributor to the increasing greenhouse effect, have been the aim of extensive research to avoid permanent damage to the climate system. The combustion of fossil fuel for energy generation is recognized as the dominant source of anthropogenic CO₂ emission. CO₂ removal and storage is a practical option that has the possibility to decrease CO₂ emission from large fixed industrial stations.1,2 Among different techniques suggested for CO₂ capture including chemical and physical absorption, adsorption, membrane, and cryogenic processes, amine scrubbing is a robust, matured, appropriate, and popular technology that is in use from 1930 and could apply to conventional power plants.3 Nevertheless, it has some issues such as corrosion, amine losses, and high energy requirement for solvent regeneration.4 Consequently, more research is required to improve the process and solvents. Compared to amines, Pz has been presented to have many beneficial qualities containing low thermal and oxidative degradation rates,5,6 the low regeneration energy,7,8 the fast CO₂ absorption rate, and low corrosivity relative to widely used monoethanolamine (MEA), diethanolamine, and other amines.9 Furthermore, Pz displays a relatively high absorption rate.10 In recent research, the stirrer bubble column is applied to the amine-based CO₂ absorption processes.11−14 A bubble column is used in diverse industrial processes owing to the simple design, great heat- and mass-transfer performance, and intricate hydrodynamic attribute. However, the scale-up and design of this equipment are very laborious due to its complicated hydrodynamic. The absorption performance of the system is a complex dependent on layout, scheme, and operating parameters such as column construction, sparger characteristic, type and speed of stirrer, the flow rate of liquid and gas, CO₂ partial pressure, and amine loading. Therefore, a good understanding of the complex relationship between the effective factors is essential to optimize the process. In light of these concerns, a systematic approach is particularly significant to evaluate the true potential of this technology and indicate the influence of key parameters on its performance.

Response surface methodology (RSM) is a time-consuming and powerful statistical technique that could be applied to optimize and model a wide range of engineering systems.15 This method includes experimental design, which systemati-
cally reduces the number of tests, and numerous regression assessment to attain the conditions that resulted in the best answer about the studied empirical range. RSM is an effective tool for simultaneous consideration independent variables and their interactions that affect the objective function where a reply of profits is impressed by numerous factors. The target response is approximated with a polynomial equation in which its coefficients describe the effect of corresponding variables, and also this mathematical model is a guide to optimization search.

Newly, several articles published about the usage of RSM regarding the preparation of CO2 solid sorbents, and the other studies are focused on optimizing the CO2 absorption process. The performance of commercial active carbon for CO2 removal from simulated shifted-syngas flow was studied using full factorial and central composite designs (CCDs). Nuchitprasittichai and Cremaschi applied RSM to the simulation of the CO2 capture process in amine-based process to identify the design variables and optimal operating conditions which yield the least costly of the process. Also, to evaluate the quality of RSM results, they compared it with an artificial neural network (ANN) and concluded that the RSM models could predict the optimal solutions which are close to the ones obtained by ANN. Morero et al. used RSM to evaluate the performance of the different solvents in the absorption–desorption biogas upgrading process. The effects of temperature, total pressure, amount of CO2, circulation rate, and their interactions on use energy, recovery of CH4, and CO2 capture were determined. Babamohammadi et al. employed a CCD to present a quadratic model for CO2 solubility in a blended solution based on MEA amount, temperature, concentration of glycerol, and gas flow rate. The obtained results revealed that amine concentration is the most effective parameter on the objective function. Table 1 demonstrates the recent studies on using RSM to optimize the CO2 capture process.

In the present research, the principal objective was to investigate the effect of the modification parameters, Pz concentration, liquid flow rate, CO2 flow rate, and speed of stirrer, on the CO2 absorption performance such as CO2 loading, CO2 removal efficiency, absorption rate, and NCO2 of the modified absorption in a stirrer bubble column. Because the design and evaluation of statistical tests can be used for process modeling and optimization, the RSM based on the CCD was used to design experiments and also developing the quadratic equation models that would predict the optimum conditions for desirable responses. Up to now, no analysis has been done on the optimization of absorption performance by Pz–H2O–CO2 in the stirrer bubble column using the RSM approach. The main feature of the bubble column is its absorption performance which is strongly affected by the operating conditions. For the analysis of the optimization for the operating condition of the Pz–H2O–CO2 system, the method of experimental design was applied. To comprehend the interactions between the variables, the statistical model has been developed. To discover the optimum condition and the processes optimization under which the finest conceivable response has been investigated, RSM is the best-fitted statistical method and the experiment numbers needed are decreased due to the use of it.

2. MATERIALS AND METHOD

2.1. Materials. In this research, the aqueous Pz solution was used as an absorbent to study of the CO2 absorption performance. The liquid chemical solvent was acquired from Merk Co., Germany with the >99% purity, and the solvent without extra purification was applied. To prepare the desirable aqueous solutions (0.1, 0.2, 0.3, 0.4, and 0.5 M), double-distilled water was used. The Testo 327-1, Germany gas analyzer, was applied to analyze the value of CO2 gases in the outlet of the column. The CO2 gas cylinder (99.999% purity) was prepared from Hor Mehr Tab Gas Co. and was used a compressor (300 l capacity, AP-301, Mahak) to the preparation of the air. Two flow meters were used to measure carbon dioxide and air in the entrance in term of L/min. The CO2 concentration was revolving from 12 to 44% by volume.

2.2. Apparatus and Procedure. Figure 1 displays the schematic diagram of 10 cm ID and 38 cm height bubble column equipped with a mixer, a distributor of 30 mm height and 75 mm OD, and a manometer to set the liquid volume. The distributor holes were 1.0 mm ID and inclusive of six holes. The fresh Pz solution is fed into a feed tank. Then, the feed is fed into the upper column. The fresh solution was passed through the flow meter and the appropriate amount of liquid has been set to 3.0 l with a manometer in all experiments. The flow rate of solution and concentration of Pz solution ranges were 0.5 to 2.5 L/h and 0.1 to 0.5 M, respectively. The mixer was applied to improve the absorption time and contact area of bubbles and liquid in the far away areas of the column. For this purpose, a dimmer was used to set and control the stirrer speed. CO2 and air were released from the compressor and high purity cylinder, respectively, and carried to the bubble column with a separate flow meter. The individual regulator has been used to regulate CO2 and air pressure. The CO2 and mixed gas flow rate ranges were 0.6–2.2 and 5.0 L/min, respectively. Also, the electrical heating was applied to prohibit the hydrate formation in the gas pipeline. All tests were performed at ambient temperature, and atmospheric pressure. The CO2 unabsorbed was measured continuously by an analyzer in the treated discharge column.

2.3. Experiments Design. One of the suitable tools for analysis, assessment, and modeling of the result of different operating variables on the interaction is RSM. RSM was developed by Box and Behnken. This expression was emanated of the graphical point of view created since the adaptability with the mathematical model, and its application has been extensively expressed in chemo-metrics contexts. RSM includes statistical methods and mathematical groups that are obtained from experimental models to fit the empirical data in communication to the experimental setup. To this end, the functions of quadratic polynomial were employed to explain the work studied. Several steps in the RSM usage such as an optimization method (Figure 2) are as follows: (1) the experimental design selection and carrying out the experiments due to the choice of the empirical matrix; (2) the election of independent variables from the large results on the process via the empirical region definition and screening studies, according to the study purpose and the researcher experience; (3) the statistical–mathematical processing of the experimental data created via the appropriate polynomial model; (4) the model’s fitness assessment to experimental data; (5) the urgent confirmation and replacement feasibility.
Table 1. Some Studies on the CO₂ Absorption Performance Using RSM Techniques*  

| sorbent                      | variables | response | design            | model                                                                 | R²    | Adj R² | ref. |
|------------------------------|-----------|----------|-------------------|----------------------------------------------------------------------|-------|--------|------|
| TEPA, DEA, MSU-F             | C<sub>TEPA</sub>, C<sub>DEA</sub>, C<sub>MCH</sub> | q<sub>CO₂</sub> | full factorial, CCD | Y = 5.62192 + 0.0830368X₁ − 0.0345798X₂ − 0.0208987X₃ − 0.156322X₄ − 0.619369X₅ − 0.140222X₆ − 0.295X₇ − 0.215X₈ − 0.1375X₉ | 0.953 | 0.995  | 19   |
| activated carbon             | T<sub>act</sub>, P<sub>CO₂</sub> | q<sub>CO₂</sub>, t<sub>b</sub> | full factorial | Q = 2.14E + 0.0487T + 2.128P<sub>CO₂</sub> − 0.01097P<sub>CO₂</sub> + 0.000317 + 0.106P<sub>CO₂</sub>² | 0.999 | 0.998  | 26   |
| activated carbon             | T<sub>act</sub>, D<sub>act</sub> | q<sub>CO₂</sub> | full factorial | Y = −20.4159 + 0.06687T + 0.21348B − 0.00027T² − 0.000047B² − 0.0016B² | 0.970 | 0.949  | 20   |
| activated carbon             | T<sub>act</sub>, P<sub>CO₂</sub> | q<sub>CO₂</sub>, t<sub>b</sub> | full factorial | capture capacity = 3.1210 − 0.07797T + 0.8067P<sub>CO₂</sub> + 0.0067T² | 0.982 | 0.969  | 16   |
| activated carbon             | T<sub>act</sub>, P<sub>CO₂</sub> | q<sub>CO₂</sub>, t<sub>b</sub> | full factorial | T<sub>b</sub> = 8.042 + 0.239T + 2.4067P<sub>CO₂</sub> + 0.0202T² | 0.991 | 0.984  | 16   |
| TEPA, b-CHT                   | α<sub>TEPA</sub>C<sub>CO₂</sub> T, W/F ratio | q<sub>CO₂</sub> | face-CCD, full factorial | Y = 5.65 + 0.37A + 0.23B + 0.23C + 0.47D − 0.17B + C − 0.26B + D + 1.3D² | n.d. | 0.917  | 28   |
| HMPD, AEEA                   | P<sub>CO₂</sub>, CHMPD, CAEEA | α<sub>CO₂</sub> absorption rate | n.d. | (CO₂ loading) | n.d. | 0.962  | 29   |
| MEA, glycerol                | C<sub>MEA</sub>C<sub>glycerol</sub> T, Q<sub>q</sub> | α<sub>CO₂</sub> | CCD | Ln(R<sub>α</sub>) = −5.73021 + 0.63342A + 1.84441B + 5.19352 + 3.5474X1 + 0.15605B − 0.04215C + 1.72213X1 + 0.035598A + B + 7.8927X1 + 10³A | 0.969 | 0.967  | 25   |
| DGA, DEP                   | P, T, P<sub>CO₂</sub> | q<sub>CO₂</sub>, Q<sub>d</sub>, Q<sub>loading</sub> | CCD | power requirement = +76783.4 + 49159.26A + 33099.96B + 25702.65AB | 0.999 | 0.998  | 24   |
| MEA, DGA DEA, MDEA, TEA      | n<sub>act</sub>, C<sub>act</sub>, C<sub>DEA</sub>, C<sub>MCH</sub> | q<sub>CO₂</sub> capture, T<sub>act</sub>, Q<sub>act</sub> | full factorial, Box–Behnken | Y<sub>θ</sub> = 78.12 + 2.96x₁ + 0.57x₂ + 0.79x₃ + 1.24x₄ + 1.49x₅ − 0.29x₁x₂ + 0.8x₁x₃ | n.d. | 0.961  | 18   |
| aminated activated carbons   | n<sub>act</sub>, C<sub>act</sub>, C<sub>DEA</sub>, C<sub>MCH</sub> | q<sub>CO₂</sub>A<sub>CO₂</sub> | CCD | Y<sub>θ</sub> = 93.7 − 2.6x₁ − 0.48x₂ − 0.25x₃ + 1.36x₄ + 0.86x₅ + 0.19x₁x₃ − 0.33x₁x₃ | n.d. | 0.988  | 22   |

* n.d. = not defined.
a substitution in orientation to the optimal; and (6) optimizing the value of each studied variables.

In the current work, to specify the optimum levels, the CCD of RSM was applied. CCD can be used to extend response models of second-order with finite factor numbers \( n \) (2 < \( n \) < 6). According to the CCD, the design of experiments was applied to extend an RSM by quadratic approximation model. In this work, the RSM together with the CCD was applied to simulate the CO\(_2\) absorption process. The four major independent variables, namely, liquid and CO\(_2\) flow rate, concentration of Pz, and speed of stirrer were considered. The all four independent variables parameter were considered at five various levels \((- \alpha, -1, 0, +1, +\alpha)\). These factors were selected on the basis of our previous literature\(^{12,41,42}\) and operated in the range of 0.1 to 0.5 M, 0.5 to 2.5 l/h, 1 to 2.2 l/min, and 0 to 400 rpm, respectively. According to available studies on CO\(_2\) absorption, the operating conditions and the levels of the considered variable for the CCD runs were selected and are introduced in Table 2.

Therefore, the following quadratic equation was used with four independent variables:\(^{18,43}\)

\[
Y = \beta_0 + \sum_{i=1}^{4} \beta_i X_i + \sum_{i=1}^{4} \beta_{ii} X_i^2 + \sum_{i=1}^{4} \sum_{j=i+1}^{4} \beta_{ij} X_i X_j + \varepsilon
\]

(1)

where \( Y \) is the response function that is predicted (i.e., CO\(_2\) removal efficiency), \( \beta_0 \) represents the constant term (offset), \( \beta_i \) and \( \beta_{ii} \) express the coefficient of the linear and quadratic result, respectively, \( X_i \) and \( X_j \) represent the coded value of variable \( i, j \), and \( \beta_{ij} \) express the interaction coefficient effect, and \( \varepsilon \) represents the unanticipated parameters related to the experiments.\(^{20,39}\)

The analysis of multiple regressions of the experimental data to fit eq 1 was used by the applying the least-squares method, which it causes to generate the \( \beta \) coefficients with the least possible residual. The model acquired explains the response behavior in the empirical area as an independent variable agent. The CO\(_2\) capture based on the modified Solvay method

Table 2. Range and Level of Independent Variables for CCD Runs\(^a\)

| factors                | tag   | symbol | units | level          | level          | level          | level          | level          |
|------------------------|-------|--------|-------|----------------|----------------|----------------|----------------|----------------|
|                        |       |        |       | \(+\alpha\)    | \(-1\)         | \(0\)          | \(+1\)         | \(+\alpha\)    |
| Pz concentration       | \(C_{Pz}\) | \(X_1\) | M     | 0.1            | 0.2            | 0.3            | 0.4            | 0.5            |
| liquid flow rate       | \(Q_l\) | \(X_2\) | l/h   | 0.5            | 1.0            | 1.5            | 2.0            | 2.5            |
| gas flow rate          | \(Q_{CO2}\) | \(X_3\) | l/min | 0.6            | 1.0            | 1.4            | 1.8            | 2.2            |
| stirrer speed          | \(w\) | \(X_4\) | rpm   | 0              | 100            | 200            | 300            | 400            |

\(^a\alpha = 2\) (axial point or star for orthogonal CCD about four independent variables).
was optimized using RSM. Numerical optimization was followed by analyzing the critical factors and their interactions. The design of runs was in accordance with CCD. The reaction time was considered in a screening survey and set to be 2 h because maximum CO₂ capture was not at this time. The optimal liquid and gas flow rate, P2 concentration, and speed of stirrer speed for CO₂ capture have been found by the response optimizer.

After obtaining information about each empirical level of the selected plan, it is essential to explain the response treatment similar to the values points study to fit a mathematical equation. That’s mean; there must be estimates the parameters b from the eq 1. Therefore, in the notation of matrix, eq 1 can be express as

\[ y_{ni} = X_{ni}b + e_{ni} \]

where \( X \) is the chosen experimental design matrix, \( e \) is the residual, \( y \) and \( b \) are the response and the model parameter vectors, respectively, and \( m \) and \( n \) indicate the lines and columns numbers from the matrices, respectively. Equation 2 is solved by utilizing a statistical method named the method of least square. The least-square method is a regression skill exploited to fit a model to a set of empirical data producing the best residual feasible. In the following, because mathematical alteration in eq 2, a vector \( b \) can be calculated as

\[ b_{n-1} = (X_{ni}^TX_{ni})^{-1}X_{ni}^Ty_{ni} \]

The mathematical model can sometimes rarely examine the experimental domain after fitting the performance with the data. The further reliable method to appraise the model quality is using of analysis of variance (ANOVA). The ANOVA main mentality is to contrast the change because of the variation of the variable amount combined with the change because of accidental errors intrinsic to the generated errors as a result of the response computations. From this analogy, it is practicable to consider the regression importance applied to anticipate answers to evaluate the empirical variance origins. In the ANOVA, the diversity of the datasets is evaluated with a multiple regression equation (SSreg) and the residuals produced with the model (SSres), as demonstrated below

\[ SS_{lof} = \sum_{i=1}^{n} \sum_{j=1}^{m} (\hat{y}_{ij} - \bar{y})^2 \]

An estimate of the de

\[ SS_{res} = \sum_{i=1}^{n} \sum_{j=1}^{m} (\hat{y}_{ij} - \bar{y})^2 \]

Similarly, the pure error sum of the square (SSpe) and the lack of fit sum of the square (SSlof) can be calculated as

\[ SS_{lof} = \sum_{i=1}^{n} \sum_{j=1}^{m} (\hat{y}_{ij} - \bar{y})^2 \]

where, \( y_{ij} \) is the experiment numbers and \( p \) is the number of model parameter; \( \bar{y}, \) overall media; \( \hat{y}_{ij} \), estimated value for the level \( i \) by the model; \( y_{ij} \), repeats media carried out in the same set of empirical conditions. \( y_{ij} \), repeats performed in each single levels.

The all sum of the square seeing deflections in communication with the media is named the total sum of the square (SSreg); it may be differentiated in the sum of the square because of the coordinated model, in this way, because of the regression (SSreg) and the residuals produced with the model (SSres), as demonstrated below

\[ SS_{res} = SS_{pe} + SS_{lof} \]

As the central point repeats are created, it can be feasible to assess the net error related to replication. Afterward, the residuals sum of the square can be divided into two parts: the pure error sum of the square (SSpe) and the lack of fit sum of the square (SSlof), as demonstrated below

\[ SS_{res} = SS_{pe} + SS_{lof} \]

During the sum of the square division for all variation, origin (residual, regression, pure, total, and lack of fit error) is created with its degrees of freedom (d.f.)-related numbers; the “media of the square” (MS) are acquired. The degree of freedom numbers for these variation origins are computed by the statements demonstrated in Table 3, where \( p \) is the number of

| variation source | sum of the square | degree of freedom |
|------------------|------------------|------------------|
| regression       | \( SS_{reg} \)   | \( p-1 \)         |
| residuals        | \( SS_{res} \)   | \( n-p \)         |
| lack of fit      | \( SS_{lof} \)   | \( m-p \)         |
| pure error       | \( SS_{pe} \)    | \( n-m \)         |
| total            | \( SS_{tot} \)   | \( n-1 \)         |

\( m \), total levels number in the plan; \( n \), observations number; \( p \), number of model parameter; \( \bar{y}, \) overall media; \( y_{ij} \), estimated value for the level \( i \) by the model; \( y_{ij} \), repeats media carried out in the same set of empirical conditions. \( y_{ij} \), repeats performed in each single levels.

The determination coefficient corrected with the absolute average deviation (AAD) and variables number (Adj-\( R^2 \)) was deliberated in order to survey the model correctness. Adj-\( R^2 \) should be near to 1.0 and the AAD should be as small as feasible between the observed and predicted. Adj-\( R^2 \) indicates the ratio of data variables defined by the model. The AAD represents the deviations between the calculated and empirical values and it is calculated by the following equation means

\[ AAD = \frac{100}{n} \sum_{i=1}^{n} \left( \frac{|y_{i,exp} - y_{i,cal}|}{y_{i,exp}} \right) / n \]

where \( n \) is the number of data points and \( y_{i,exp} \) and \( y_{i,cal} \) are the experimental and calculated responses, respectively.

Occasionally, a small subset of the data has a disproportionate effect on the regression model. In other words, predicting or estimating parameters probably depends more on the influential subset than the majority data. Some parameters are used to influence diagnostics through the following equations.

\[ \hat{y} = X\hat{b} \]
\[ \epsilon = Y - \hat{y} \]

where, \( y_{ij} \), \( \hat{y} \), and \( \epsilon \) are the measured response data, the predicted value from the model, and error value, respectively. Leverage \( (h_{ij}) \) is the ability of a design point to impression the model coefficients fit, given their position in the design space.
Leverage is a point that varies from 0 to 1 and shows how much a design point influences the model’s values. A leverage of 1 means that the predicted and experiments value are exactly equal, that is, the residual will be 0.

$$H = X(X'X)^{-1}X' = [h_{ii}]$$ (10)

where $X$ and $H$ are the model matrix of $n$ rows and $p$ columns and an $n \times n$ symmetric matrix, respectively. The diagonal elements of the $H$ matrix are the leverages. Leverage indicates the fraction of the error variance, along with the point approximated, and carried into the model. The numbers of estimated standard deviations separating the actual and predicted values named internally studentized residual as

$$r_i = \frac{e_i}{\hat{\sigma}\sqrt{1 - h_{ii}}}, \quad i = 1, 2, 3, \& n$$ (11)

The externally studentized residual was computed by leaving each run, out of the analysis, one at a time and estimating the response from the remaining runs.

$$\hat{\sigma}_{(-i)}^2 = \frac{(n - p)\sigma^2 - \frac{e_i^2}{1 - h_{ii}}}{\sigma\sqrt{1 - h_{ii}}}, \quad i = 1, 2, 3, \& n$$ (12)

where $n$ and $p$ are the number of runs minus the one being left out and the number of terms in the model including the intercept, respectively. The $t$-value was defined as the number of standard deviations difference between the actual response and predicted value. A value associated with the $t$-distribution that measures the number of standard deviations separating the parameter estimates from zero.

$$t_i = \frac{e_i}{\hat{\sigma}_{(-i)}\sqrt{1 - h_{ii}}}, \quad i = 1, 2, 3, \& n$$ (13)

DFFITS is the studentized difference between the predicted value without observation $i$ and the predicted value with observation $i$ that defined as

$$\text{DFFITS} = \frac{\hat{Y} - \hat{Y}_{(-i)}}{\hat{\sigma}_{(-i)}\sqrt{1 - h_{ii}}}$$ (14)

where

$$\hat{Y}_{(-i)} = Y + \frac{e_i}{1 - h_{ii}}$$ (15)

DFFITS is a statistical measure of impression based on the different in coefficients of model (betsas) that occurs when a run is removed and displays the impression the $ith$ seeing has on each regression coefficient. The DFFITSA is the standard errors number that the $ith$ model coefficient alters if the $ith$ observation is deleted. A great value of DFFITSA infers that the $ith$ seeing has further effect on the $jth$ coefficient.

$$\text{DFFITSA}_{j(-i)} = \frac{\hat{\beta}_j - \hat{\beta}_{j(-i)}}{\sqrt{\hat{\sigma}_{(-i)}^2(X'X)^{-1}}}$$ (16)

Cook’s distance ($D_i$) is a square yield of a monotonic function of the leverage and the $ith$ internally studentized residual.\(^22\)

$$D_i = \frac{r_i^2}{p + 1\left(\frac{h_{ii}}{1 - h_{ii}}\right)}$$ (17)

The equation above represents that $D_i$ contains the squared studentized residual, which indicates how well the model fits the $ith$ observation $y_i$ and a component that measures how far that point is from the rest of the data. If the value of $D$ is significantly less than 1, omitting the $ith$ case cannot change the regression coefficients estimated very well.

### 3. THEORETICAL BASIS

CO₂ removal efficiency determined as the mole of CO₂ captured per moles of CO₂ loaded to the column is as follows\(^36,47\)

$$\text{CO}_2 \text{ removal efficiency} = R = \frac{\chi_{\text{CO}_2,\text{in}} - \chi_{\text{CO}_2,\text{out}}}{\chi_{\text{CO}_2,\text{in}}} \times 100$$ (18)

where $\chi_{\text{CO}_2,\text{in}}$ and $\chi_{\text{CO}_2,\text{out}}$ are CO₂ removal efficiency, mole fraction of CO₂ in inlet and outlet columns, respectively, and $R$ is the CO₂ removal efficiency. The bubbles were supposed to be oblate-ellipsoidal and specified by the minor axis ($e$) and major axis ($E$). The dimensions a bubble relevant with a diameter equivalent to a sphere with the same ellipsoid volume was calculated as follows\(^36,49\)

$$d = \sqrt[3]{\frac{\pi}{6}}$$ (19)

The volume surface mean diameter or Sauter mean diameter ($d_{32}$) was determined with the data computed to get an adequate diameter by means of eq 20.\(^36\)

$$d_{32} = \frac{\sum_{i=1}^{N} n_i d_i^3}{\sum_{i=1}^{N} n_i d_i^2}$$ (20)

where $n_i$ is the bubbles number which have an equivalent diameter $d_i$. The changing the volume in the column was specified by the seeing of the fluid level and the alteration generated when the gas phase is existing. The gas holdup ($e_G$) was computed by the expansion method of volume (eq 21).\(^32\)

$$e_G = \frac{\Delta V}{\Delta V + V_i}$$ (21)

where $V_i$ is the volume of liquid before the gas entrance and $\Delta V$ is the solution volume expansion after the gas is blown through the liquid, computed from the liquid level change. The volume variation of gas–liquid dispersion was observed with respect to the seeing changes in the liquid level and its increase after entering the gas. Thus, the specific interfacial area was calculated by using the gas holdup and the Sauter mean diameters as eq 22.\(^36\)

$$a = \frac{e_G}{d_{32}(1 - e_G)}$$ (22)

The gaseous mixture (air–carbon dioxide) was blown through the sparger disc into the liquid phase, and the liquid is conducted through the counter-currently. In all experiments, the absorption performance was done in 1 h, and it was assumed that the liquid phase does not enter the gases, and the air was not solved in the solution. The CO₂ absorption rate ($\Delta G$) can be easily calculated as the competition in CO₂.
concentration through the column at the pressure and temperature constant with the following equation

$$\Delta G = \rho_{g,\text{in}} Q_{g,\text{in}} \left( \frac{\chi_{\text{CO}_2,\text{in}} - \chi_{\text{CO}_2,\text{out}}}{1 - \chi_{\text{CO}_2,\text{out}}} \right)$$

(23)

where $\rho_{g,\text{in}}$ and $Q_{g,\text{in}}$ are the density of inlet gases and inlet gas flow rate, respectively. Also, $\chi_{\text{CO}_2,\text{in}}$ and $\chi_{\text{CO}_2,\text{out}}$ are the CO₂ mole fraction in the inlet and outlet of the column, respectively. In each test, different points of data are prepared in a steady-state flux with different partial pressures of the gas phase. Because it is hard to obtain the concentration of CO₂ in a steady-state phase. Because it is hard to obtain the concentration of CO₂ in

The following expression and equilibrium CO₂ partial pressure of the liquid phase ($P_{\text{CO}_2,*}$) were used. The CO₂ mass-transfer flux ($N_{\text{CO}_2}$) into the aqueous Pz solution at the bubble column is given by the expression

$$N_{\text{CO}_2} = \frac{n}{V \times a} = K_G (P_{\text{CO}_2,b} - P_{\text{CO}_2,*})$$

(24)

where $P_{\text{CO}_2,b}$ and $P_{\text{CO}_2,*}$ are the partial pressure of CO₂ in the gas phase and solution bulk, respectively. And also, $K_G$ is the overall mass-transfer coefficient. At the above equation, the pressure difference term can be expressed using the log mean average CO₂ partial pressure at the inlet and outlet columns

$$\Delta p_{\text{CO}_2,\text{in}} = \frac{P_{\text{CO}_2,\text{in}} - P_{\text{CO}_2,\text{out}}}{\ln \left( \frac{P_{\text{CO}_2,\text{in}}}{P_{\text{CO}_2,\text{out}}} \right)}$$

(25)

Because the solution or equilibrium CO₂ partial pressure is unknown, the amount of $P_{\text{CO}_2,*}$ term in the case of CO₂ unloaded absorbent can be omitted. Therefore, the log mean average CO₂ partial pressure will be equal $P_{\text{CO}_2,b}$. Thus, the overall mass transfer coefficient, $K_G$, can be calculated by the following expression

$$K_G = \frac{N_{\text{CO}_2}}{\Delta p_{\text{CO}_2,\text{in}}}$$

(26)

4. REACTION KINETICS

According to our previous studies, numerous chemical reactions happen in a bubble column. The possible reactions are summarized in Table 4.

For kinetic evaluation of the system, the understanding of all species concentration in the solution is required. The details and calculation method are in our previous work. The CO₂ loading ($a_{\text{CO}_2}$) is used to compare the amount of CO₂ absorption in the solution and this parameter is determined as follows

$$a_{\text{CO}_2} = \frac{C_{\text{CO}_2} + C_{\text{HCO}_3^-} + C_{C\text{O}_2\text{H}^-} + C_{\text{PZCOO}^-} + C_{\text{PZ\text{H}COO}^-} + 2C_{\text{PZ\text{HCOO}^-}}}{C_{\text{PZ}} + C_{\text{PZH}^+} + C_{\text{PZCOO}^-} + C_{\text{PZ\text{H}COO}^-} + C_{\text{PZ\text{HCOO}^-}}}$$

(27)

5. RESULT AND DISCUSSION

5.1. Design of Experiment and Statistical Analysis Method. The RSM was used to analyze the effect of several parameters on the CO₂ absorption performance. The

independent level variables are the different values that should be determined by the experiments. All these independent variables were examined at five levels. Before applying the RSM, an experimental plan was selected that specified what tests must be done in the experimental area under survey as a set of various combinations of the independent variable levels. In this study, the effect of the four variables [$P$ concentration ($X_1$), liquid flow rate ($X_2$), CO₂ flow rate ($X_3$), and stirrer speed ($X_4$)] on the CO₂ absorption process was appraised in terms of CO₂ loading, CO₂ removal efficiency, and $N_{\text{CO}_2}$. This includes 30 tests, which are demonstrated in Table 5, consisting of 24 factorial points and 6 additional repeats at the design center in which it was conceivable to approximate the experimental error related by the replications.

The RSM suggested a quadratic model that relates for four CO₂ absorption processes to the independent variables (eqs 28–31 in Table 7). The CO₂ removal efficiency, CO₂ loading, CO₂ absorption rate, and $N_{\text{CO}_2}$ are the response, and $X_1$, $X_2$, $X_3$, and $X_4$ are the coded terms of the investigated parameters. The value and sign of each correlation phrase coefficient display the decreasing and increasing effects of the response parameters. Given the proposed correlation for CO₂ removal efficiency, the relative significance of the independent agents are as follows: $X_1$ (i.e., $P$ concentration) with value of −1.31 for the coefficient, $X_2$ (i.e., liquid flow rate) with value of −5.03 for the coefficient, $X_3$ (i.e., CO₂ flow rate) with value of +3.11 for the coefficient, and $X_4$ (stirrer speed) with value of +2.12 for the coefficient. The maximum increasing impact of the dependent factor is +2.06 that is related to the interaction between $X_1$ and $X_3$ parameters. The coded factors in the quadratic model can be applied to forecast the response levels given by each agent. By default, the low levels and upper levels of the factors are coded as −2 and +2, respectively. The equations of coded were beneficial for knowing the relative effect of the parameters by comparing the coefficient of factors. The equation of regression for the response variables in coded terms acquired from the empirical data based on the interaction influences between the factors is shown in Table 6.

5.2. Analysis of Variance (ANOVA). ANOVA and the statistical parameters for the CO₂ removal efficiency, CO₂ loading and $N_{\text{CO}_2}$ from the CCD are presented in Table 8.
The lack of a considerable regression and a no considerable result on the response for CO₂ removal efficiency, CO₂ loading, and N$_{CO₂}$ were obtained to be 12.8, 1193.38, and 96.62, respectively.$^{55}$ Moreover, the model term has a considerable result on the response because of the large F-value. The F-value for three CO₂ removal efficiency, CO₂ loading, and N$_{CO₂}$, were obtained to be 12.8, 1193.38, and 96.62, respectively, which points that the models are meaningful. There is only less than 0.01% probability that this large amount of F-value may occur because of noise.

5.3. Fit Statistics. It can be derived from the determination coefficient (R$^2$ = 0.945, 0.999, and 0.992 for CO₂ removal efficiency, CO₂ loading and N$_{CO₂}$, respectively), which indicates that the data fit the model very well. Namely, 94.5, 99.9, and 99.2% of the total variation of CO₂ removal

## Table 5. Coded and Actual Values of the Variables Used to Design the Experiment

| run no. | X₁ | X₂ | X₃ | X₄ | % R | α | N$_{CO₂}$ | run no. | X₁ | X₂ | X₃ | X₄ | % R | α | N$_{CO₂}$ |
|---------|----|----|----|----|-----|---|----------|---------|----|----|----|----|-----|---|----------|
| 1       | 0  | 0  | 0  | 0  | 73.6 | 0.053 | 9.52     | 16      | −1 | −1 | −1 | −1 | 76.8 | 0.072 | 12.30    |
| 2       | 0  | 0  | 0  | 0  | 73.7 | 0.056 | 9.43     | 17      | 2  | 0  | 0  | 0  | 78.4 | 0.041 | 12.42    |
| 3       | −1 | −1 | −1 | 1  | 72.6 | 0.097 | 6.34     | 18      | 1  | −1 | −1 | −1 | 75.9 | 0.082 | 10.18    |
| 4       | 0  | 0  | 0  | 0  | 73.8 | 0.054 | 9.53     | 19      | 1  | −1 | −1 | −1 | 76.2 | 0.080 | 10.09    |
| 5       | 1  | −1 | 1  | 1  | 76.2 | 0.870 | 11.70    | 20      | −1 | 1  | 1  | 1  | 77.6 | 0.099 | 11.82    |
| 6       | 0  | 0  | 0  | 0  | 73.8 | 0.054 | 9.46     | 21      | 0  | 2  | 0  | 0  | 80.4 | 0.078 | 12.56    |
| 7       | −1 | −1 | −1 | −1 | 73.6 | 0.530 | 9.24     | 22      | 1  | 1  | −1 | −1 | 81.2 | 0.056 | 13.11    |
| 8       | 0  | 0  | 0  | 2  | 73.1 | 0.520 | 9.13     | 23      | 0  | −2 | 0  | 0  | 73.8 | 0.052 | 9.93     |
| 9       | −1 | 1  | −1 | −1 | 74.5 | 0.580 | 9.27     | 24      | 1  | 1  | −1 | −1 | 78.1 | 0.048 | 11.61    |
| 10      | 0  | 0  | 0  | 0  | 73.7 | 0.055 | 9.44     | 25      | 0  | 0  | 0  | −2 | 73.1 | 0.049 | 9.22     |
| 11      | 1  | 1  | 1  | 1  | 76.7 | 0.048 | 11.80    | 26      | −2 | 0  | 0  | 0  | 70.2 | 0.152 | 8.84     |
| 12      | 1  | −1 | 1  | −1 | 78.6 | 0.069 | 14.20    | 27      | 1  | 1  | 1  | −1 | 80.2 | 0.047 | 12.86    |
| 13      | 0  | 0  | 0  | 0  | 73.8 | 0.055 | 9.45     | 28      | 0  | 0  | 2  | 0  | 77.2 | 0.056 | 10.22    |
| 14      | −1 | −1 | 1  | 1  | 77.4 | 0.054 | 13.70    | 29      | −1 | 1  | 1  | −1 | 80.9 | 0.072 | 14.20    |
| 15      | 0  | 0  | −2 | 0  | 70.5 | 0.041 | 6.80     | 30      | −1 | 1  | −1 | −1 | 79.6 | 0.680 | 13.70    |

The unit of α and N$_{CO₂}$ are mol/mol, and mol/m²s, respectively.

## Table 6. Estimated Coefficients in Terms of Coded Factors

| term     | % R | Loading, mol/mol | ΔG, g/min | N$_{CO₂}$, mol/m²s |
|----------|-----|------------------|-----------|--------------------|
| constant | +78.86 | +0.0678 | 1.86 | +0.0110 |
| X₁       | −1.31 | −0.0792 | −0.0435 | +0.0002 |
| X₂       | −5.03 | −0.0149 | −0.1363 | −0.0005 |
| X₃       | +3.11 | +0.0208 | 0.8288 | +0.0044 |
| X₄       | +2.12 | +0.0053 | 0.0572 | +0.0002 |
| X₁X₂     | +2.06 | +0.0003 | 0.0529 | −0.0001 |
| X₁X₃     | +0.1150 | −0.0083 | 0.0250 | +0.0002 |
| X₁X₄     | −1.01 | −0.0030 | −0.0281 | −0.0003 |
| X₂X₃     | +0.0000 | +0.0000 | 0.0000 | +0.0000 |
| X₂X₄     | −2.96 | −0.0015 | −0.0787 | −0.0002 |
| X₃X₄     | +0.0000 | +0.0000 | 0.0000 | +0.0000 |
| X₁²      | +1.35 | +0.0522 | 0.0389 | +0.0000 |
| X₂²      | +4.71 | +0.0136 | 0.1291 | +0.0007 |
| X₃²      | −0.4716 | +0.0012 | 0.0608 | +0.0000 |
| X₄²      | −2.24 | −0.0008 | −0.0599 |     |

## Table 7. Equations in Terms of Coded Factors

| parameter                        | correlation                                                                 |
|----------------------------------|-----------------------------------------------------------------------------|
| CO₂ removal efficiency           | 78.86 − 1.31X₁ − 0.03X₂ + 3.11X₁ + 2.12X₂ + 0.06X₃X₁ + 0.015X₂X₃ |
| CO₂ loading (mol/mol)            | −0.0678 − 0.0792X₁ − 0.0149X₂ + 0.0208X₃ + 0.0053X₄ + 0.0003X₁X₂ |
| absorption rate                  | −0.0083X₁X₃ − 0.0030X₁X₄ − 0.0015X₂X₄ + 0.0522X₂² + 0.0136X₄² |
| mass transfer flux (mol/m³s)     | + 0.0012X₁² − 0.0008X₂² |
|                                  | 1.86 − 0.0435X₁ − 0.0163X₂ + 0.8288X₃ + 0.057X₄ + 0.0529X₁X₂ |
|                                  | + 0.068X₁² − 0.0599X₂² |
|                                  | 0.0110 + 0.0002X₁ − 0.00005X₂ + 0.0044X₃ + 0.0002X₄ − 0.0001X₁X₂ |
|                                  | + 0.0002X₁X₃ − 0.0003X₂X₄ − 0.0002X₃X₄ + 0.0007X₄² |
Table 8. ANOVA Results and Statistical Parameters of the Developed Quadratic Correlation Versus; Concentration of Pz ($X_1$), Solution Flow Rate ($X_2$), CO2 Flow Rate ($X_3$), and Speed of Stirrer ($X_4$)

| Source          | CO2 removal efficiency | CO2 loading, mol/mol | $N_{CO2}$ mol/m^2·s |
|-----------------|------------------------|----------------------|----------------------|
|                 | sum of squares | degree of freedom | mean square | F-value | p-value | sum of squares | degree of freedom | mean square | F-value | p-value | sum of squares | degree of freedom | mean square | F-value | p-value |
| model           | 159.36     | 12                   | 13.28       | 12.8    | 0.003    | 0.0435    | 12               | 0.0036       | 1193.3     | <0.0001  | 0.0001   | 12               | 8.786 × 10^{-6} | <0.0001    |         |
| $X_1$           | 1.68       | 1                    | 1.68        | 1.6     | 0.2345   | 0.0062    | 1                | 0.0062       | 2036.3     | <0.0001  | 4.198 × 10^{-8} | 1               | 4.198 × 10^{-8} | 0.461       | 0.5139  |
| $X_2$           | 5.01       | 1                    | 5.01        | 4.8     | 0.0556   | 0.0000    | 1                | 0.0000       | 14.5       | 0.0041   | 4.718 × 10^{-6} | 1               | 4.718 × 10^{-6} | 0.518       | 0.4896  |
| $X_3$           | 21.82      | 1                    | 21.82       | 21.0    | 0.0013   | 0.0010    | 1                | 0.0010       | 320.8      | <0.0001  | 0.0000   | 1                | 0.0000       | 480.6       | <0.0001  |
| $X_4$           | 8.24       | 1                    | 8.24        | 7.9     | 0.0201   | 0.0001    | 1                | 0.0001       | 16.9       | 0.0026   | 6.620 × 10^{-6} | 1               | 6.620 × 10^{-6} | 0.728       | 0.4156  |
| $X_1X_2$        | 0.8166     | 1                    | 0.8166      | 0.787   | 0.3981   | 1.594 × 10^{-8} | 1                | 1.594 × 10^{-8} | 0.005      | 0.9438   | 7.077E-10      | 1               | 7.077E-10     | 0.007       | 0.9316  |
| $X_1X_3$        | 0.0150     | 1                    | 0.0150      | 0.014   | 0.9070   | 0.0001    | 1                | 0.0001       | 25.7       | 0.0007   | 5.509 × 10^{-8} | 1               | 5.509 × 10^{-8} | 0.605       | 0.4563  |
| $X_1X_4$        | 1.87       | 1                    | 1.87        | 1.8     | 0.2124   | 0.0000    | 1                | 0.0000       | 5.3        | 0.0468   | 1.829 × 10^{-7} | 1               | 1.829 × 10^{-7} | 2.0         | 0.1898  |
| $X_2X_3$        | 0.0000     | 0                    | 0           | 0       | 0.0000   | 0.0000    | 0                | 0.0000       | 0          | 0.0000   | 0.0000   | 0                | 0.0000       | 0           | 0.0000   |
| $X_2X_4$        | 0.0000     | 0                    | 0           | 0       | 0.0000   | 0.0000    | 0                | 0.0000       | 0          | 0.0000   | 0.0000   | 0                | 0.0000       | 0           | 0.0000   |
| $X_3X_4$        | 5.13       | 1                    | 5.13        | 4.9     | 0.0533   | 1.332 × 10^{-6} | 1                | 1.332 × 10^{-6} | 0.438      | 0.5244   | 2.674 × 10^{-8} | 1               | 2.674 × 10^{-8} | 0.294       | 0.6008  |
| $X_1^2$         | 3.72       | 1                    | 3.72        | 3.6     | 0.0907   | 0.0006    | 1                | 0.0006       | 1841.8     | <0.0001  | 3.575 × 10^{-9} | 1               | 3.575 × 10^{-9} | 0.039       | 0.8472  |
| $X_2^2$         | 4.94       | 1                    | 4.94        | 4.8     | 0.0571   | 0.0000    | 1                | 0.0000       | 13.5       | 0.0051   | 1.247 × 10^{-7} | 1               | 1.247 × 10^{-7} | 1.4         | 0.2717  |
| $X_3^2$         | 0.3643     | 1                    | 0.3643      | 0.351   | 0.5681   | 2.403 × 10^{-6} | 1                | 2.403 × 10^{-6} | 0.791      | 0.3968   | 1.530 × 10^{-9} | 1               | 1.530 × 10^{-9} | 0.017       | 0.8996  |
| $X_4^2$         | 12.91      | 1                    | 12.91       | 12.4    | 0.0064   | 1.450 × 10^{-6} | 1                | 1.450 × 10^{-6} | 0.677      | 0.5069   | 1.917 × 10^{-8} | 1               | 1.917 × 10^{-8} | 0.211       | 0.6570  |
| residual        | 9.34       | 9                    | 1.04        | 0       | 0.0000   | 3.036 × 10^{-6} | 9                | 3.036 × 10^{-6} | 1.5        | 0.5504   | 6.190 × 10^{-8} | 8               | 7.737 × 10^{-9} | 0.010       | 1.0000  |
| lack of fit     | 5.69       | 8                    | 0.7116      | 0.195   | 0.9466   | 0.0000    | 8                | 3.166 × 10^{-6} | 1.5        | 0.5504   | 7.565 × 10^{-7} | 1               | 7.565 × 10^{-7} | 1.0000      |         |
| pure error      | 3.64       | 1                    | 3.64        | 2.000 × 10^{-6} | 1 | 2.000 × 10^{-6} | 0.0001    | 21               | 0.0435     | 21       | 0.0001   | 21               | 0.0001       |             |         |
efficiency, CO₂ loading, and NCO₂, respectively, were justified in reply to the offered quadratic correlation (Table 9). As

Table 9. ANOVA for Response Surface Quadratic Model

| factors        | % R | CO₂ loading, mol/mol | NCO₂, mol/m²s |
|----------------|-----|----------------------|---------------|
| R²             | 0.945 | 0.999                | 0.992         |
| adjusted R²    | 0.871 | 0.999                | 0.982         |
| predicted R²   | NA   | NA                   | NA            |
| adeq precision | 14.403 | 129.488              | 41.305        |
| std. dev.      | 1.0200 | 0.0017               | 0.0003        |
| mean           | 77.2200 | 0.0653               | 0.0120        |
| C.V. %         | 1.32 | 2.67                 | 2.51          |

*Case(s) with 1.0000 leverage: PRESS statistic and pred R² not defined. The deviation error for R², adjusted R², adeq precision are 0.0001 and deviation error for std. dev., mean, and C.V. % are 0.00001, 0.00001, and 0.001, respectively.

remarked by Joglekar and May,⁵⁶ for the data fit the model very well, the correlation coefficient must be at least 0.8. The high value of R² indicates good compatibility between the actual and calculated results within the wide range of the experiments (see Figure 3). In this work, the regression equation of the determination coefficient (R²) was above 0.94 for all three response variables, indicating that the polynomial can properly explain the communication between the interactions, factors, and response. The actual against predicted value plot for CO₂ removal efficiency rise is shown in Figure 3a. As seen in this figure, the residuals were generally placed on a straight line and normally distributed. The actual value and predicted value for all responses were close to each other (not shown). Therefore, this observation shows that these models were suitable for the empirical data, and they can be applied to the analysis and prediction of the absorption performance. The adequate precision (adeq Precision) of this correlation for CO₂ removal efficiency, CO₂ loading, and NCO₂ were 14.40, 129.49, and 41.30, respectively (adeq precision >4) that represents that the model noise ratio is located in the favorable range.³¹ A ratio or adequate precision greater than 4 is favorable. Because of the ANOVA analysis results and Figure 3a, the offered model for all three systems is valid.

As known, the residuals from the least-squares are a significant instrument for the investigation of the adequacy of the models. The hypothesis of constant variance at distinct levels was considered at Figure 3b by drawing the predicted response values versus residual as acquired from the model. As seen in these figures, there was a random distribution of points up and down the x-axis between +4.594 and −4.594 without any trends. This conclusion surveys the reliability and adequacy of the models, and a constant variance was seen through the response range. As an additional tool to check the adequacy of the final model, the normal probability chart of the studentized residuals has been shown in Figure 3c. If the model is sufficient, the points on the normal probability charts versus the residuals must form a straight line. On the other hand, as an extra useful tool to examine the suitability of the ultimate model, the normal distribution probability charts of the studentized residuals were shown in Figure 3c. If the model is sufficient, the points on the normal probability charts versus the residuals must form a straight line. In these charts, the points pursue a direct line and approving that the errors were distributed normally with mean constant and zero but unclear variance as the fundamental hypothesis of the studies. And also, the charts of different variables versus residuals such as

![Figure 3. The CCD Predicted value of CO₂ removal efficiency vs; (a) actual absorption, and (b) externally studentized residuals, and externally studentized residuals vs; (c) normal probability, and (d) number of run.](https://dx.doi.org/10.1021/acsomega.9b03363)
run order, predicted values, and factors were analyzed (not shown). There was no reason to doubt any independence contravention or hypothesis of constant variance, as all plots represented a closely permanent variance over the response ranges. Therefore, all charts seemed to be favorable and there was no reason to deny the results. Meanwhile, the residual plots for CO2 removal efficiency is shown in Figure 3d. Figure 3d is corresponding to the removal efficiency, which reveals that there was no predictable pattern observed because all the run residues lay on or between the levels of $-4.594$ to $4.594$.

5.4. Interaction of Factors. In this work, the version 11.0 of Design Expert was applied to represent three-dimensional (3-D) response surfaces and partition the dataset draws in Table 3. The 3-D curves of response surface to understand the interaction of the variable parameters (i.e., concentration of Pz, solution flow rate, CO2 flow rate, and the speed of stirrer) and to locate the best level of each variable for maximum response.
in CO₂ removal efficiency, CO₂ loading, and N₂CO₂ were drawn in Figures 4–6. And also in these figures, the plots were applied to the detection of the best range of each four variable factor. The label lines on the plot, also the various colors of the plots and response surfaces, represented a degrees variety of interaction based on the CO₂ removal efficiency, CO₂ loading, and N₂CO₂ [see eqs 28, 29 and 31]. The mutual influence of the two variable parameters on the removal efficiency was more considerable than that of the two another one showed in Figure 4. The mutual influence of the liquid flow rate and CO₂ concentration was similar to that of the Pz concentration and solution flow rate. Anyhow, the curved slope on the three-dimensional response surface (see Figure 4a,d) displayed that the concentration level of CO₂ and Pz a higher effect on the removal efficiency compared with the speed of stirrer and gas flow rate level of setup. As a result, these two parameters played an important task in impressing the CO₂ removal, which became known to be compatible with the outcomes acquired from the regression model ANOVA. In the circumstances of this research, the main reason for increasing the removal efficiency with the CO₂ flow rate comes from the increase in the number of CO₂ molecules and causes to increase the reaction between the CO₂ and free Pz molecules and leads to an increase in the CO₂ removal efficiency. On the contrary, as seen from Figure 4c, the removal efficiency was increased to an optimum value and then decreased with the increase in the speed of the stirrer. By increasing the speed of stirrer, the CO₂ bubbles were broken to the small ones and cause to increase the contact area between CO₂ and Pz molecules. But, by further increasing the stirrer speed (>200 rpm), the removal efficiency decreases due to the phenomenon of coagulation. Furthermore, according to the RSM, the removal efficiency decreased favorably (blue area in Figure 4d) when the liquid flow rate increased to a given level, which proposes that Pz concentration remaining the main parameter in controlling the CO₂ removal efficiency. According to the 3-D response surface displayed in Figures 5 and 6, Figure 5c displayed that there was a considerable relationship between the CO₂ and liquid flow rate. As seen from this figure, the mass-transfer flux was improved with increases in the CO₂ flow rate but decreases with the liquid flow rate. And also, the mass

Figure 5. Response surfaces plots of mass transfer flux as a function of (a) solution flow rate and Pz concentration, (b) CO₂ flow rate and Pz concentration, (c) CO₂ flow rate and solution flow rate, and (d) stirrer speed and CO₂ flow rate.
transfer flux attained the maximum value (approximately 0.01599 mol/m²·s) when the gas flow rate was at their maxima within the experiment boundaries. Furthermore, the interaction importance between the liquid flow rate and stirrer speed was the same as that between liquid flow rate and Pz concentration (see Figure 5a), and the mass transfer flux increased weak with continual increases in both variable parameters.

Figure 6a indicates that the loading increased and decreased with continual increases in the solution flow rate and concentration of Pz, respectively. However, it was obvious from this figure that there is the weak interaction between the CO₂ loading and liquid flow rate. Figure 6d indicates that interaction importance of CO₂ flow rate on the loading was great. By increasing the flow rate of the CO₂ because of the increase in the number of the empty CO₂ molecules in the
solution, the chemical reaction rate between the CO₂ and Pz increased and caused to increase the loading. It can be found from Figure 6e that the loading increased with the increase of the speed of stirrer because of broken bubbles to small ones and caused to increase in the contact area.

5.5. Best Absorption Operating Parameters. One of the purposes of this work was to observe independent variable (i.e., Cₚz, Q, Q, CO₂ loading, and w) combination somehow to get the maximum absorption performance. Because of the performed tests, the RSM optimization proposed various combinations of the variables to get over 95% absorption performances. In this way, an optimization run with 97.6% of CO₂ removal efficiency was selected. This optimal point can be obtained in the following conditions: 0.162 M of Pz concentration, 0.502 l/h of liquid flow rate, 2.199 l/min of CO₂ flow rate, and 68.898 rpm of stirrer speed. At optimal points, the absorption rate, CO₂ loading, and NCO₂ were obtained 2.980 g/min, 0.198 mol/mol, and 0.0164 mol/m²·s, respectively. Three repeat experiments were carried out under the suggested optimal conditions. As seen in Table 10, the average experimental was in near assent with the anticipated. On the other hands, the validity of the proposed model is confirmed again.

Using numerical optimization, a favorable value for each input parameter and response can be chosen. Here, the feasible input optimizations that can be chosen contain the minimum, maximum, range, none (for responses), target, and set so as to appont an optimized output value for a given set of conditions. In this work, the variables of input data were given to determine ranged values because the response was planned to gain a maximum. with these conditions, the maximum achieved CO₂ removal efficiency, absorption rate, loading, and mass transfer flux were 97.93%, 3.129 g/min, 0.258 mol/mol, and 0.016447 mol/m²·s, respectively (see Table 11) at above-mentioned conditions.

5.6. Deviation Plots. The deviation plot indicates the overall influence of all process parameters on the response function, and the center point (0) was the middle point of the operating range. A perturbation plot to compare the effect of all four operating parameters (Pz concentration, CO₂ and liquid flow rate and stirrer speed) at the reference points is demonstrated in Figure 7. It was observed from Figure 7a that the CO₂ loading decreases with the increase of the Pz concentration (A) and liquid flow rate (B) due to the increase of Pz in the solution. However, the reduction rate of loading was further for Pz concentration in comparison to the liquid flow rate. It is also clear that the CO₂ loading increases with an increase in the CO₂ flow rate (C) due to increase CO₂ agents in the interface and then in solution. It can be noticed that from this plot, the stirrer speed (D) has also the same effect due to the increase of the contact area because of the bubbles broken into small bubbles. It is also evident from the Figure 7b that the NCO₂ rises with the increase of the CO₂ flow rate (C) and stirrer speed (D), but the effect of the CO₂ flow rate was significant. And also, the increase of the flow rate had a negative effect and the effect of Pz concentration was low. It can be observed from Figure 7c that the effect of parameters on the CO₂ removal was the same CO₂ loading.

6. CONCLUSIONS

In this work, the influence of numerous important operating parameters such as Pz concentration, liquid flow rate, CO₂ flow rate, and speed of stirrer on CO₂ loading, CO₂ removal efficiency, and NCO₂ has been investigated. We optimized the piperazine-based CO₂ capture process to maximize the absorption performance using simulation—optimization RSM. The RSM with CCD was used to the development of appropriate model by the least-squares method. The deviation errors obtained for all absorption performance less than 0.0001 and the results were the following:

(1) From the regression analysis of variables, it has been found that the models were successfully tested and all verified with empirical data and determined the values of the optimum variables to maximize absorption performance.

(2) The model p-value for CO₂ removal efficiency, CO₂ loading, and NCO₂ were less than 0.05 and that points all three models are significant. And also, the model F-value for these three absorption performances were 12.80, 1193.38, and 96.62, respectively, and it indicates only less than 0.01% probability that this large amount of F-value may occur because of noise.

(3) The process optimization was performed and the empirical values acquired for the CO₂ capture were found to agree satisfactorily with the model values. The optimal absorption conditions were obtained at the Pz concentration of 0.1 M, solution flow rate of 0.56 l/h, mixed gas flow rate of 2.16 l/min, and stirrer speed of 298 rpm. In these conditions, the experimental yield of

Table 10. Repeatability and Validation Test for the Experimental Absorption Performance Carried Out under Optimal conditions

| RUN  | % R   | G, g/min | CO₂ loading, mol/mol | NCO₂, mol/m²·s |
|------|-------|----------|----------------------|-----------------|
| 1    | 96.8  | 2.968    | 0.197                | 0.0164          |
| 2    | 97.7  | 2.972    | 0.196                | 0.0164          |
| 3    | 97.6  | 2.974    | 0.197                | 0.0164          |

The deviation error for % R, G, CO₂ loading, and mass transfer flux are 0.01, 0.0001, 0.0001, and 0.00001, respectively.

Table 11. Optimization of the CO₂ Adsorption by RSM-CCD

| parameter and response | constrain | low | high | optimum condition |
|------------------------|-----------|-----|------|-------------------|
| Cₚz (mol/l)            | in range  | 0.1 | 0.5  | 0.152             |
| Q (l/h)                | in range  | 0.5 | 2    | 0.63              |
| Q,CO₂ (l/min)          | in range  | 1   | 2.2  | 2.16              |
| W (rpm)                | in range  | 0   | 300  | 247.9             |
| CO₂ loading (mol/mol)  | maximize  | 0.024 | 0.198 | 0.258             |
| NCO₂ (mol/m²·s)        | maximize  | 0.00636 | 0.01599 | 0.01645         |
| CO2 removal efficiency (%) | maximize | 70.64 | 82.26 | 97.93             |
CO₂ removal efficiency, CO₂ loading, and Nₐ were 97.9%, 0.258 mol/mol, and 0.0164 mol/m²·s, respectively. The results of the comparison of predictions with experimental data (% AARD = 3.78–18.14, MSE = 0–6.784 and R² = 0.855–0.953) determined that the Buckingham π theory has the potential to properly predict reactive absorption performance over a wide range of experimental conditions.

**AUTHOR INFORMATION**

**Corresponding Author**
Ahad Ghaemi — School of Chemical, Petroleum and Gas Engineering, Iran University of Science and Technology, Tehran 16846-13114, Iran; orcid.org/0000-0003-0390-4083; Email: aghaemi@iust.ac.ir

**Authors**
Hassan Pashaei — Faculty of Chemical, Petroleum and Gas Engineering, Semnan University, Semnan, Iran
Masoud Nasiri — Faculty of Chemical, Petroleum and Gas Engineering, Semnan University, Semnan, Iran; orcid.org/0000-0002-5182-6668
Bita Karami — School of Chemical, Petroleum and Gas Engineering, Iran University of Science and Technology, Tehran 16846-13114, Iran

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.9b03363

**Notes**
The authors declare no competing financial interest.

**NOMENCLATURE**

| Symbol | Description |
|--------|-------------|
| a | specific gas–liquid area, m²/m³ |
| AEEA | aminoethylethanolamine |
| C₈ | total CO₂ concentration, mol/l |
| C₈ | total Pz concentration, mol/l |
| d | diameter of equivalent sphere, mm |
| d₃₂ | Sauter mean diameter, cm |
| DEA | diethanolamine |
| DEPG | dimethyl ethers polyethylene glycol |
| DGA | diglycolamine |
| HMPD | 4-hydroxy-1-methylpiperidine |
| Kᵢ₆ | total gas phase mass transfer coefficient, kmol/m²·s·kPa |
| MDEA | N-methyldiethanolamine |
| MEA | monoethanolamine |
| MSU-F | mesostructured cellular silica foam |
| Nₐ | mass transfer flux, mol/m²·s |
| P | total system pressure, kPa |
| P₈ | inlet CO₂ partial pressure, kPa |
| P₈ | outlet CO₂ partial pressure, kPa |
| P₈ | partial pressure of CO₂, kPa |
| P₈ | gas bulk partial pressure of CO₂, kPa |
| P₈ | piperazine |
| Q₈ | CO₂ flow rate, l/min |
| Q₈ | gas flow rate, l/min |
| P₈ | equilibrium CO₂ partial pressure of the bulk solution, kPa |
| P₈ | interface partial pressure of CO₂, kPa |
| Q₈ | solution flow rate, l/h |
| Q₈ | reboiler duty |

Figure 7. Deviation curves for responses with coded factors; (a) CO₂ loading, (b) mass transfer flux, and (c) CO₂ removal efficiency.
TEA  triethylenetetramine
TEPA  tetraethylpentamine
TEPA/b-cHT  tetraethylpentamine-functionalized basic-modified calcined hydrotalcite

\( T \)  temperature, K
\( W \)  total mass fraction
\( y_{\text{CO}_2,\text{in}} \)  mole fraction of inlet \( \text{CO}_2 \)
\( y_{\text{CO}_2,\text{out}} \)  mole fraction of outlet \( \text{CO}_2 \)

**GREEK LETTERS**

\( \alpha_{\text{CO}} \)  \( \text{CO}_2 \) loading, mol \( \text{CO}_2/\text{mol Pz} \);
\( \rho_\ell \)  density of liquid, kg/m\(^3\);
\( \rho_g \)  density of gas, kg/m\(^3\);
\( \varepsilon_{\text{GH}} \)  gas holdup; \( \Delta G \)  absorption rate, g/min

**REFERENCES**

(1) Nejat, P.; Jomehzadeh, F.; Taheri, M. M.; Gohari, M.; Abd. Majid, M. Z. A global review of energy consumption, CO2 emissions and policy in the residential sector (with an overview of the top ten CO2 emitting countries). *Renew. Sustain. Energy Rev.* 2015, 43, 843–862.

(2) Wennersten, R.; Sun, Q.; Li, H. The future potential for Carbon Capture and Storage in climate change mitigation—an overview from perspectives of technology, economy and risk. *J. Clean. Prod.* 2015, 103, 724–736.

(3) Rochelle, G. T. Amine scrubbing for CO2 capture. *Science 2009*, 325, 1652–1654.

(4) Amiri, M.; Shahhosseini, S. Optimization of CO2 Capture from Simulated Flue Gas Using K2CO3/Al2O3 in a Micro Fluidized Bed Reactor. *Energy Fuels 2018*, 32, 7978–7990.

(5) Bougie, F.; Iluuta, M. C. CO2 absorption in aqueous piperazine solutions: experimental study and modeling. *J. Chem. Eng. Data 2011*, 56, 1547–1554.

(6) Plaza, J. M.; Chen, E.; Rochelle, G. T. Absorber intercooling in CO2 absorption by piperazine-promoted potassium carbonate. *AIChE J. 2009*, 56, 905–914.

(7) Costa, C.; Demartini, M.; Di Felice, R.; Oliva, M.; Pagliai, P. Piperazine and methyldiethanolamine interrelationships in CO2 absorption by aqueous amine mixtures. Part I: Saturation rates of single-reactant solutions. *Can. J. Chem. Eng. 2019*, 97, 1160–1171.

(8) Yarveyc, H.; Ghiasi, M. M.; Mohammadi, A. H. Performance evaluation of the machine learning approaches in modeling of CO2 equilibrium absorption in piperazine aqueous solution. *J. Mol. Liq. 2018*, 255, 375–383.

(9) Stowe, H. M.; Paek, E.; Hwang, G. S. First-principles assessment of CO2 capture mechanisms in aqueous piperazine solution. *Phys. Chem. Chem. Phys. 2016*, 18, 25296–25307.

(10) Conway, W.; Fernandes, D.; Beyad, Y.; Burns, R.; Lawrance, G.; Puxty, G.; Maeder, M. Reactions of CO2 with aqueous piperazine solutions: formation and decomposition of mono-and dicarbamic acids/carbamates of piperazine at 25.0 °C. *C. J. Phys. Chem. A 2013*, 117, 806–813.

(11) Pashaei, H.; Ghaemi, A.; Nasiri, M. Modeling and experimental study on the solubility and mass transfer of CO2 into aqueous DEA solution using a stirrer bubble column. *RSC Adv. 2016*, 6, 108075–108092.

(12) Pashaei, H.; Ghaemi, A.; Nasiri, M. Experimental investigation of CO2 removal using Piperazine solution in a stirrer bubble column. *Int. J. Greenhouse Gas Control 2017*, 63, 226–240.

(13) Pashaei, H.; Zarandi, M. N.; Ghaemi, A. Experimental study and modeling of CO2 absorption into diethanolamine solutions using a stirrer bubble column. *Chem. Eng. Res. Des. 2017*, 121, 32–43.

(14) Pashaei, H.; Zarandi, M. N.; Ghaemi, A. Experimental study and modeling of CO2 absorption into diethanolamine solutions using a stirrer bubble column. *Chem. Eng. Res. Des. 2017*, 121, 32–43.

(15) Mäkelä, M. Experimental design and response surface methodology in energy applications: a tutorial review. *Energy Convers. Manage. 2017*, 151, 630–640.

(16) García López, S.; Gil Matellanes, M. V.; Fernández Martín, C.; Pís Martínez, J. J.; Rubiera González, F.; Peviá García, C. Breakthrough adsorption study of a commercial activated carbon for pre-combustion CO2 capture. *Chem. Eng. J. 2011*, 171, 549.

(17) Song, C.; Kitamura, Y.; Li, S. Optimization of a novel cryogenic CO2 capture process by response surface methodology (RSM). *J. TaiwanInst. Chem. Eng. 2014*, 45, 1666–1676.

(18) Nuchiprasittichai, A.; Cremaschi, S. Optimization of CO2 capture process with aqueous amines using response surface methodology. *Comput. Chem. Eng. 2011*, 35, 1521–1531.

(19) Dao, D. S.; Yamada, H.; Yogo, K. Response Surface Optimization of Impregnation of Blended Amines into Mesoporous Silica for High-Performance CO2 Capture. *Energy Fuels 2015*, 29, 985–992.

(20) Gil, M. V.; Martínez, M.; García, S.; Rubiera, F.; Pís, J. J.; Peviá, C. Response surface methodology as an efficient tool for optimizing carbon adsorbents for CO2 capture. *Fuel Process. Technol. 2013*, 106, 55–61.

(21) Gil Matellanes, M. V.; Martínez Fernández, M.; García López, S.; Rubiera González, F.; Pís Martínez, J. J.; Peviá García, C. Response surface methodology as an efficient tool for optimizing carbon adsorbents for CO2 capture. *Fuel Process. Technol. 2013*, 106, 55–61.

(22) Shafeeyan, M. S.; Wan Daud, W. M. A.; Houshmand, A.; Arami-Niya, A. The application of response surface methodology to optimize the amination of activated carbon for the preparation of carbon dioxide adsorbents. *Fuel 2012*, 94, 465–472.

(23) Nuchiprasittichai, A.; Cremaschi, S. Optimization of CO2 Capture Process with Aqueous Amines: A Comparison of Two Simulation–Optimization Approaches. *Ind. Eng. Chem. Res. 2013*, 52, 10236–10243.

(24) Morero, B.; Groppelli, E. S.; Campanella, E. A. Evaluation of biogas upgrading technologies using a response surface methodology for process simulation. *J. Clean. Prod. 2017*, 141, 978–988.

(25) Babamohammadi, S.; Shamiri, A.; Nejad Ghaffar Borhani, T.; Shafeeyan, M. S.; Aroua, M. K.; Yusoff, R. Solubility of CO2 in aqueous solutions of glycerol and monoethanolamine. *J. Mol. Liq. 2018*, 249, 40–52.

(26) Karimi, M.; Silva, J. A. C.; Díaz de Tuesta, J.; Rodrigues, A. E.; Gomes, H. T.; Gomes, H. T. CO2 Capture in Chemically and Thermally Modified Activated Carbons Using Breakthrough Measurements: Experimental and Modeling Study. *Ind. Eng. Chem. Res. 2018*, 57, 11154–11166.

(27) García, S.; Gil, M. V.; Pís, J. J.; Rubiera, F.; Peviá, C. Cyclic operation of a fixed-bed pressure and temperature swing process for CO2 capture: Experimental and statistical analysis. *Int. J. Greenhouse Gas Control 2013*, 12, 35–43.

(28) Thouchiprasittichai, N.; Pintuyothin, N.; Pongstrobodee, S. Optimization of CO2 adsorption capacity and cyclical adsorption/desorption on tetraethylpentamine-supported surface-modified hydrotalcite. *J. Environ. Sci. 2018*, 65, 293–305.

(29) Maleki, N.; Motahari, K. Absorption performance of carbon dioxide in 4-Hydroxy-1-methylpiperedine- aminomethyl ethanolamine aqueous solutions: Experimental measurement and modeling. *J. Nat. Gas Sci. Eng. 2018*, 56, 1–17.

(30) Myers, R. H.; Montgomery, D. C.; Anderson-Cook, C. M. Response Surface Methodology: Process and Product Optimization Using Designed Experiments; John Wiley & Sons, 2016.

(31) Ölmaz, T. The optimization of Cr (VI) reduction and removal by electrocoagulation using response surface methodology. *J. Hazard. Mater. 2009*, 162, 1371–1378.

(32) Körbalt, B. K.; Rauf, M. A. Application of response surface analysis to the photolytic degradation of Basic Red 2 dye. *Chem. Eng. J. 2008*, 138, 166–171.

(33) Khuri, A. I.; Mukhopadhyay, S. Response surface methodology. *Wiley Interdiscipl. Rev. Comput. Stat. 2010*, 2, 128–149.

(34) Ahmad, A. A.; Hameed, B. H. Effect of preparation conditions of activated carbon from bamboo waste for real textile wastewater. *J. Hazard Mater. 2010*, 173, 487–493.
(35) Gilmour, S. G. Response surface designs for experiments in bioprocessing. *Biomass Bioenergy* **2006**, *62*, 323–331.

(36) Bruns, R. E.; Scarminio, I. S.; de Barros Neto, B. Statistical Design-Chemometrics; Elsevier, 2006; Vol. 25.

(37) Teófilo, R. F.; Ferreira, M. *Quimiotermia II: planilhas eletrônicas para cálculos de planejamentos experimentais, um tutorial*; Química Nova, 2006.

(38) Sadeghi, N.;Sharifinia, S.; Do, T.-O. Optimization and modeling of CO2 photoconversion using a response surface methodology with porphyrin-based metal organic framework. *React. Kinet. Mech. Catal.* **2018**, *125*, 411–431.

(39) Mourabet, M.; El Rhilassi, A.; El Boujaady, H.; Bennani-Ziatni, M.; Taitai, A. Use of response surface methodology for optimization of fluoride adsorption in an aqueous solution by Brushite. *Arabian J. Chem.* **2017**, *10*, S3292–S3302.

(40) Amiri, M.; Shahhosseini, S.; Ghaemi, A. Optimization of CO2 capture process from simulated flue gas by dry regenerable alkali metal carbonate based adsorbent using response surface methodology. *Energy Fuels* **2017**, *31*, S286–S296.

(41) Pashaei, H.; Ghaemi, A.; Nasiri, M.; Heydari, M. Experimental investigation of the effect of nano heavy metal oxide particles in Piperazine solution on CO2 absorption using a stirrer bubble column. *Energy Fuels* **2018**, *32*, 2037.

(42) Heydari, M.; Pashaei, H.; Ghaemi, A.; Nasiri, M. Reactive absorption of CO2 into Piperazine aqueous solution in a stirrer bubble column: Modeling and experimental. *Int. J. Greenhouse Gas Control* **2018**, *79*, 91–116.

(43) Wang, C.; Wei, A.; Wu, H.; Qu, F.; Chen, W.; Liang, H.; Li, G. Application of response surface methodology to the chemical cleaning process of ultrafiltration membrane. *Chin. J. Chem. Eng.* **2016**, *24*, 651–657.

(44) Zhang, Y.-j.; Li, Q.; Zhang, Y.-x.; Wang, D.; Xing, J.-m. Optimization of succinic acid fermentation with Actinobacillus succinogenes by response surface methodology (RSM). *J. Zhejiang Univ. - Sci. B Biomed. Biotechnol.* **2012**, *13*, 103–110.

(45) Baş, D.; Boyacı, I. H. Modeling and optimization I: Usability of response surface methodology. *J. Food Eng.* **2007**, *78*, 836–845.

(46) Yeh, J. T.; Pennline, H. W.; Resnik, K. P. Study of CO2 absorption and desorption in a packed column. *Energy Fuels* **2001**, *15*, 274–278.

(47) Hairul, N. A. H.; Shariff, A. M.; Bustam, M. A. Mass transfer performance of 2-amino-2-methyl-1-propanol and piperazine promoted 2-amino-2-methyl-1-propanol blended solvent in high pressure CO2 absorption. *Int. J. Greenhouse Gas Control* **2016**, *49*, 121–127.

(48) Jia, X.; Hu, W.; Yuan, X.; Yu, K. Effect of surfactant type on interfacial area and liquid mass transfer for CO2 absorption in a bubble column. *Chin. J. Chem. Eng.* **2015**, *23*, 476–481.

(49) López, A. B.; La Rubia, M. D.; Navaza, J. M.; Pacheco, R.; Gómez-Díaz, D. Carbon dioxide absorption in triethanolamine aqueous solutions: hydrodynamics and mass transfer. *Chem. Eng. Technol.* **2014**, *37*, 419–426.

(50) Mouza, A. A.; Dalakoglou, G. K.; Paras, S. V. Effect of liquid properties on the performance of bubble column reactors with fine pore spargers. *Chem. Eng. Sci.* **2005**, *60*, 1465–1475.

(51) Edali, M.; Idem, R.; Aboudheir, A. 1D and 2D absorption-rate/kinetic modeling and simulation of carbon dioxide absorption into mixed aqueous solutions of MDEA and PZ in a laminar jet apparatus. *Int. J. Greenhouse Gas Control* **2010**, *4*, 143–151.

(52) Norouzbahari, S.; Shahhosseini, S.; Ghaemi, A. CO2 chemical absorption into aqueous solutions of piperazine: modeling of kinetics and mass transfer rate. *J. Nat. Gas Sci. Eng.* **2015**, *26*, 1059–1067.

(53) Jaynapathirana, C.; Shahidi, F. Optimization of extraction of phenolic compounds from wheat using response surface methodology. *Food Chem.* **2005**, *93*, 47–56.

(54) Khodaei, B.; Sobati, M. A.; Shahhosseini, S. Optimization of ultrasound-assisted oxidative desulfurization of high sulfur kerosene using response surface methodology (RSM). *Clean Technol. Environ. Policy* **2016**, *18*, 2677–2689.

(55) Montgomery, D. C.; Runger, G. C. *Applied Statistics and Probability for Engineers*; John Wiley & Sons, 2010.

(56) Joglekar, A. M.; May, A. T.; Graf, E.; Saguy, I. Product excellence through experimental design. *New Food Product and Development: From Concept to the Marketplace*; CRC Press, 1987; p 211.