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The effect of solid adsorbents in Triethanolamine (TEA) solution for enhanced CO_2 absorption rate

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Abstract

This study aimed to investigate CO_2 absorption using chemical solvent of amine H_2O-TEA-CO_2 in presence of activated carbon (AC) particles. The studied experimental range includes the temperature in range of 293–333 K, pressure in range of 3.5–9.5 bar, the concentration of solvents in range of 2.5–8.5 wt%, and amount of activated carbon in range of 0.3–0.9 kg/m^3. The central composite design (CCD) with four parameters of temperature, pressure, amine concentration, and active carbon was applied in 5 levels. The physical solubility CO_2 in amine solutions decreases with the increasing temperature that indicates the process is exothermic. The optimal values of temperature, pressure, concentration, and active carbon are 303.0 K, 8.00 bar, 7.00 M, 0.75 g, respectively, and 25.99% for the input variables and desirability index of 0.732. The CO_2 loading, absorption capacity, and absorption percentage are obtained in the range of 0.572–1.180 mol_{CO2}/mol_{TEA}, 0.208–0.506 wt%, and 12.73–32.61% in Triethanolamine (TEA) solutions in activated carbon, respectively. All dependent variables had a p value of less than 0.05, indicating that models were significant and substantial. The result showed that the addition of solid particles to chemical solvents effectively enhances CO_2 absorption.

Keywords Absorption · Carbon dioxide · Triethanolamine · Activated carbon

Introduction

The rise of carbon dioxide in global warming has become one of the most challenging topics in the environment and geology. Carbon dioxide, along with other greenhouse gases, creates an effect called the greenhouse effect. Therefore, solving this problem requires serious attention. Global warming and climate change have prompted international attempts to minimize carbon dioxide levels in the

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atmosphere [1–8]. Chimneys emitted into the atmosphere from various industries include approximately 80 % nitrogen, 15 % CO_2, 5 % oxygen, 500 ppm of sulfur dioxide, 100 ppm of carbon monoxide, and 50 ppm of methane, of which CO_2 is the most effective. It is about 55% of the current global warming. Therefore, CO_2 removal and storage are the methods that can be used to reduce greenhouse gas emissions, as it shows the highest reduction in CO_2 emissions from fossil fuel sources [9–11]. For economic and environmental reasons, researchers have paid close attention to removing CO_2 from different gas streams, especially flue gas. Currently, chemical absorption of CO_2 with alkanolamines is the most common commercial method of high-efficiency separation in the industry. Chemical absorption by amine solvents is a reliable, well-established, and practical technique widely regarded as the most selective and promising of the various CO_2 removal technologies [12–16]. Conventional amine absorbents, on the other hand, have a significant energy demand for solvent regeneration. Much effort has been made in this regard to reduce CO_2 desorption energy consumption. The most common strategy is the producing of energy-efficient solvents with more desirable properties [17–20]. Compared to monoethanolamine, tertiary amines have better thermodynamic properties and have lower regeneration energy and higher CO_2 absorption potential [20]. However, they still have limitations that can be reduced by adding solid particles such as activated carbon to amines [21, 22]. Monoethanolamine (MEA), diethanolamine (DEA), and triethanolamine (TEA) are formed when the NH_3 molecule reacts with one, two, or three ethylene oxide molecules at 50-70 bars and 350-700 ˚C [23].

Type tertiary amines, including triethanolamines, are common amines for the study of carbon dioxide capture [24–26]. Saha et al. have studied the rate of CO_2 uptake in aqueous solvents of MEA, and DEA in the presence of activated carbon particles. These experiments carried out at a temperature of 302 K, a pressure of 101.103 kPa, and a concentration of 0.1 Kmol/m^3 MEA and DEA solvents at 80 min. In all solvents used, the addition of activated carbon particles increases the rate of CO_2 uptake; also, with increasing the amount of activated carbon, the maximum adsorption rate increases. Activated carbon particles on MEA solvent had a positive effect on increasing the adsorption rate compared to the other two solvents [22]. Response surface methodology (RSM) is a process modeling and optimization technique that can be used in the design and statistical evaluation of experiments [27]. As a result, RSM based on central composite architecture was used to design experiments, construct models, and calculate the optimum modification circumstances for desirable responses in the current study. Several researches have recently been written about the use of RSM in the production of CO_2 solid sorbents [28–32]. In 1930, TEA solution was the first commercial solution of alkanolamine to be used in the gas sweetening industry and was later replaced by solutions of MEA, DEA, and other amines. Type tertiary amines have less affinity for acidic gases than type primary and type secondary amines and are therefore rarely used in gas purification processes. The only advantage of TEA over other amines is its selectivity for CO_2 and H_2S absorption. Since TEA is a tertiary amine with a high spatial barrier around the nitrogen atom, it is not capable of strong interaction and chemical bonding with CO_2, and as a result, TEA solutions containing CO_2 can be easily

and energy-efficient. Less recycled and reused than conventional industrial amines, which is of great economic importance [33].

This study aimed to investigate CO_2 uptake using the chemical solvent amine with and without activated carbon particles. Insufficient experimental data on loading and the amount of CO_2 absorption with amine solvent in the presence of physical adsorbents are not available in the sources and more on its absorption rate has been investigated. In the present study, experiments have been performed using amine solvents in the presence and absence of activated carbon particles in different ranges of different concentrations and operating conditions so that we can witness simultaneous chemical absorption and surface absorption with selected physical adsorbents and by analyzing them. The role of effective parameters is examined and analyzed, and more results are obtained in this field. The use of RSM and finding the optimal conditions to achieve the maximum load are other achievements of this research that are not mentioned in other available sources. The main method of capturing CO_2 is by absorption by amines. Amine-functionalized solid adsorbents have almost completely replaced liquid phase adsorption technology due to their recyclability and reuse, greater stability, and lower pollution.

Materials and methods

The molecular formula of TEA is $C_6H_{15}NO_3$] with a purity of 98% was purchased from Merck Industrial Corporation. CO_2 (> 99%) was supplied by Mehrabad Gas Company, Iran, and applied as adsorbate gas without more purification. Activated carbons with particle sizes ranging from 0.5 to 2.2 mm were supplied from the Iranian market. The absorbent solution was prepared with double distilled water with total solids of less than 0.1 mg.L.

The effects of the process parameters on CO_2 absorption were studied using a stainless steel reactor is shown in Fig. 1. The method of performing this test is similar to Karbalaei et al. methods [27]. This test uses a 165 mm batch reactor vessel equipped with a temperature with a thermocouple, pressure sensor, and magnetic stirrer. After preparing an aqueous solvent solution with a known weight percentage of TEA solvent and after homogenization, 20 ml of this solution is pouring into the existing tube and add a certain amount of activated carbon into a solution, is placed in the reactor. The temperature and pressure were adjusted to the desired values using digital controllers.

The experiments are carried out in various operational parameters including pressure in range of 3.5–9.5 and temperature in range of 293–333 K.

In the following equations, the absorption percent and the amount of CO2 absorbed were calculated.

$$n_{CO_2} = \frac{\left(P_{CO_2,i} - P_{CO_2,f}\right)V}{RTz} \tag{1}$$

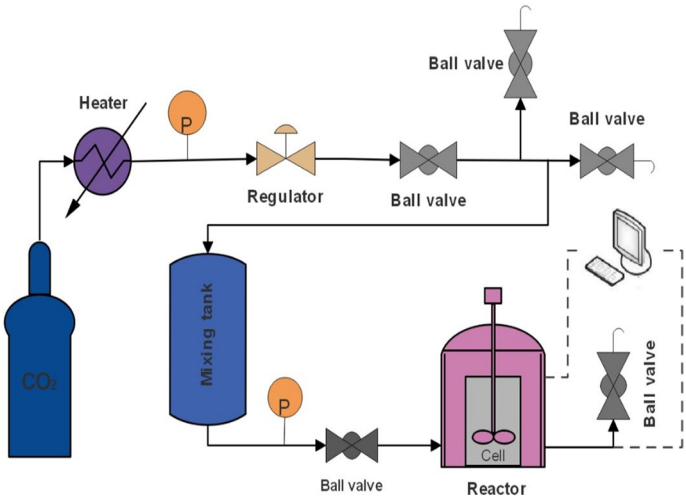

Fig. 1 A Schematic of the adsorption setup

$$Absorption(\%) = \frac{\left(P_{CO_2,i} - P_{CO_2,f}\right)}{P_{CO_2,i}} \times 100 \tag{2}$$

where $P_{CO2,i}$ represents the initial pressure, and $P_{CO2,f}$ represents the final pressure. CO_2 loading is defined as the moles of CO_2 absorbed to the moles of adsorbent with Eq. (3).

$$CO_2 \text{ loading} = \frac{n_{CO_2}}{n_{a\min e}} \tag{3}$$

namine is the mole number of amine in the liquid phase. The mole number of amine in the liquid phase is n_{amine}. CO2 is capturing with the amine during the carbonation reaction. The compressibility factor was determined using the virial equation, with cutoff coefficients greater than the second order taken into consideration. The Tsonopoulos equations (Eqs. 4, 5, 6, 7) were also used to calculate virial coefficients:

$$Z = 1 + BP \tag{4}$$

$$\frac{BP_c}{RT_c} = F^{(0)}\left(T_R\right) + \omega F^{(1)}\left(T_R\right) \tag{5}$$

$$F^{(0)}\left(T_R\right) = 0.1445 - \frac{0.330}{T_R} - \frac{0.1385}{T_R^2} - \frac{0.0121}{T_R^3} - \frac{0.000607}{T_R^8} \tag{6}$$

$$F^{(1)}(T_R) = 0.0637 + \frac{0.331}{T_R^2} - \frac{0.423}{T_R^3} - \frac{0.008}{T_R^8} \tag{7}$$

where B, Pc, Tc, and TR are the second coefficient of virial, critical pressure of CO_2, critical temperature, and reduced temperature, respectively. Coefficient of determination has become one of the most common and accurate methods for analyzing experimental data from the absorption process. The variance of the mean is represented by the coefficient of determination (R^2). The following is the coefficient of determination (R^2):

$$R^2 = \frac{\sum_{i=1}^{n}\left(qe, mes - \overline{qe, \mathrm{mod}}\right)^2}{\sum_{i=1}^{n}\left(qe, mes - \overline{qe, \mathrm{mod}}\right)^2 + \sum_{i=1}^{n}(qe, mes - qe, \mathrm{mod})^2} \tag{8}$$

where n is the number of experimental data, the mod and mes indices refer to the predicted and measured absorption values of the model, respectively. $\overline{qe, mod}$ is the average value of the experimental data [36].

TEA-H_2O-CO_2 system

In the molecular structure of TEA, the hydrogen atom is not attached to the nitrogen. Therefore, CO_2 does not react directly with it, and if water is not in the solvent, the third type of amine cannot react with CO_2. CO_2 first reacts with water to form bicarbonate. However, bicarbonate formation is slow, and this limits the reaction of CO_2 with the amine. If there is not enough water in the solvent, CO_2 will rarely be hydrated, and bicarbonate formation will be negligible [37].

$$\text{Water dissociation}: \quad 2H_2O \overset{K_1}{\longleftrightarrow} H_3O^+ + OH^- \tag{9}$$

$$CO_2\text{hydrolysis}: \quad CO_2 + 2H_2O \overset{K_2}{\longleftrightarrow} H_3O^+ + HCO_3^- \tag{10}$$

$$\text{Bicarbonate dissociation}: \quad HCO_3^- + H_2O \overset{K_3}{\longleftrightarrow} H_3O^+ + CO_3^{-2} \tag{11}$$

$$\text{TEA protonation}: \quad H_3O^+ + TEA \overset{K_4}{\longleftrightarrow} H_2O + TEAH^+ \tag{12}$$

Mechanism of CO_2 absorption enhanced by AC

In the CO_2 adsorption reaction, functional groups on the surface of carbon materials, such as amines and hydroxyl groups, play a crucial role [38]. Certain functional groups, like as alkyl-amines, can be added to a variety of porous solid materials, enhancing their CO_2 sorption characteristics and making them suitable for low-pressure captures. These amine-based adsorbents are now very common for CO_2 capture

statements because they offer rapid CO_2 adsorption rates, high adsorption capacities, and desired desorption features like facile regeneration There are numerous ways for grafting amine groups onto the surface of activated carbon (AC) to increase its CO_2 adsorption capability [39]. The adsorption mechanism for adsorbents such as reactive carbon is reactive (15). CO_2 adsorption is done by establishing covalent bonds between the adsorbent and CO_2 and establishing polar-ionic or polar-polar bonds. Therefore, in physical adsorption, the size of the molecules plays a major role in adsorption in the porous medium. No reaction occurs in this case, and as a result, the amount of energy required to reduce the adsorbent will be less [40]. The mechanism of CO_2 absorption into TEA solution is shown in Fig. 2.

$$CO_2 + Surface \Leftrightarrow (CO_2).(Surface) \tag{13}$$

RSM modeling

Researchers have paid careful attention to the response surface technique in recent years [41–44]. The answer surface method is a system of statistical and mathematical techniques for analyzing experimental outcomes. In situations where many input variables influence the process's performance and response characteristics, response surface methodology is used. A formal definition of a method necessitates the use of a polynomial function of degree 2 or higher. Since operating conditions can be linked to changes, the nonlinear second-order model can describe them. Equation 14 is a quadratic regression model that can be considered [44, 45].

$$y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \sum_{j=1}^{k} \beta_{ij} X_i X_j \sum_{i=1}^{k} \beta_{ii} X_i^2 + \varepsilon \tag{14}$$

y is the process response, i and j are the factor index numbers, and Xi and Xj are the design variables. In Eq. (4), β_0 a constant term, β_i,, and β_j are the coefficients of linear parameters, β_{ij} are the coefficients of interactive parameters, β_{ii}, and βjj are the coefficients of the quadratic parameters and ε the remaining error [35]. CCD design with these four parameters [temperature (A), pressure (B), Amin concentration (C) active carbon] was in 5 levels (Table 1). The number of tests performed by RSM for this solvent in the presence of activated carbon solid particles based on the

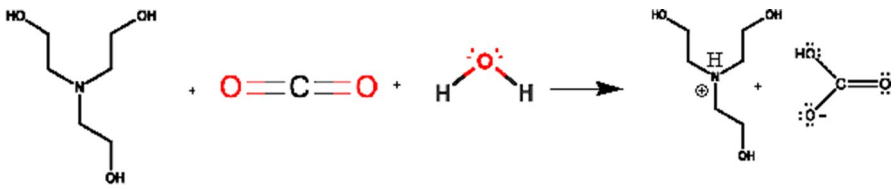

Fig. 2 Mechanism of CO_2 absorption into TEA solution

Table 1 RSM molding (Levels and parameters used in designing experiments)

Factors	Name	Symbol	Units	Coded Level				
				−2	−1	0	+1	+2
Temperature	T	A	°C	30	35	40	45	50
Pressure	P	B	bar	5	6	7	8	9
Amin concentration	C	C	mol/lit	4	4.5	5	6	7
Active carbon	m	D	gr	0.45	0.50	0.55	0.60	0.75

specified parameter range was equal to 30 runs with six replications for the center point (Table 2).

Results and discussion

Response Surface Methodology (RSM)

The number of tests performed by RSM for this solvent in the presence of activated carbon solid particles based on the specified parameter range was equal to 30 runs with six replications for the center point (Table 2). The coefficient guesstimate reflects the predicted change in answer per unit change in factor value when all remaining variables are kept constant (Table 3). In an orthogonal design, the intercept is the overall average response of all the runs. The coefficients are variations based on the factor settings around the average. The VIFs are 1 when the factors are orthogonal; VIFs greater than 1 imply multi-colinearity; the higher the VIF, the more extreme the factor association. VIFs of less than ten are considered tolerable.

The F value of 273.31 shows that the model is statistically significant [41]. An F value of this magnitude has a 0.01 percent probability of occurring due to noise. Based on the p value column of Table 4, the model p value is less than 0.001, which indicates that the model terms are of great significant [41]. In this process, terms A, B, C, D, AB, AC, A^2, and C^2 are effective parameters. Model terms with P values less than 0.0500 are significant [45]. A, B, C, D, AB, AC, A^2, and C^2 are significant model terms in this case. The model reduction can improve the model if there are many nominal model terms (not counting those needed to backing hierarchy). The F value of 3.15 for the lack of fit indicates that the lack of fit is not significant compared to the pure error [45]. There is a 10.85 percent risk that a significant "Lack of Fit F value" is caused by noise [41]. To be the model to fit, so a non-significant lack of fit is appropriate. For the obtaining response level to be acceptable, it is necessary for R^2adj and R^2pred to be greater than 0.5, which are equal to 0.9924 and 0.9796 for the quadratic model, respectively, and are within the desired range. The value of R^2 for the model is equal to 0.9961, which is close to 1 and is appropriate and reasonable. It is preferable to have a ratio of more than four. The signal-to-noise ratio of 61.466 suggests a good signal. In this section, a quadratic polynomial model is used to analyze the results. The final equation obtained according to Eq. (12–14) is

Table 2 Experimental values of the design and response of adsorption experiments

		Factor 1	Factor 2	Factor 3	Factor 4	Response 1	Response 2	Response 3
Std	Run	A:T	B:P	C:Camin	D:m	R	Loading	C_{CO2}
		C	bar	W%	gr			
21	22	40	6.5	2.5	0.60	13.97	1.1	0.208
3	4	30	8.0	4.0	0.45	16.91	1.1	0.340
1	21	30	5.0	4.0	0.45	21.42	0.9	0.284
11	10	30	8.0	4.0	0.75	17.88	1.2	0.354
9	24	30	5.0	4.0	0.75	21.70	1.0	0.290
4	9	50	8.0	4.0	0.45	12.73	0.8	0.238
2	29	50	5.0	4.0	0.45	17.80	0.7	0.220
10	16	50	5.0	4.0	0.75	18.25	0.8	0.226
12	23	50	8.0	4.0	0.75	13.50	0.8	0.249
17	2	20	6.5	5.5	0.60	25.26	1.1	0.445
23	19	40	6.5	5.5	0.30	20.29	0.8	0.324
28	1	40	6.5	5.5	0.60	20.80	0.8	0.329
25	5	40	6.5	5.5	0.60	21.02	0.8	0.333
20	6	40	9.5	5.5	0.60	16.96	0.9	0.389
27	7	40	6.5	5.5	0.60	20.66	0.8	0.328
29	25	40	6.5	5.5	0.60	20.45	0.8	0.325
19	26	40	3.5	5.5	0.60	28.22	0.6	0.261
30	27	40	6.5	5.5	0.60	20.86	0.8	0.330
26	30	40	6.5	5.5	0.60	21.08	0.8	0.335
24	12	40	6.5	5.5	0.90	21.39	0.8	0.335
18	3	60	6.5	5.5	0.60	13.92	0.6	0.236
7	11	30	8.0	7.0	0.45	25.30	0.9	0.491
5	14	30	5.0	7.0	0.45	32.12	0.8	0.400
13	8	30	5.0	7.0	0.75	32.61	0.8	0.408
15	20	30	8.0	7.0	0.75	26.20	1.0	0.506
6	13	50	5.0	7.0	0.45	25.42	0.6	0.308
8	28	50	8.0	7.0	0.45	17.29	0.6	0.331
16	17	50	8.0	7.0	0.75	18.35	0.7	0.353
14	18	50	5.0	7.0	0.75	25.56	0.6	0.312
22	15	40	6.5	8.5	0.60	28.43	0.7	0.442

C_{CO2}: Concentration of TEA wt% and %R: Removal efficiency

presented according to which the predicted values were obtained. As it is known, the numerical coefficients of temperature and TEA concentration are negative, which indicates the negative effect of these parameters, as well as the numerical coefficient of the amount of activated carbon, which shows the positive influence of this parameter on CO_2 loading.

Table 3 Coefficients in terms of coded factors

Factor	Coefficient estimate	df	Standard error	95% CI low	95% CI high	VIF
Intercept	0.7975	1	0.0058	0.7852	0.8098	
A-T	−0.1281	1	0.0029	−0.1342	−0.1219	1.0000
B−P	0.0682	1	0.0029	0.0621	0.0744	1.0000
C-Camin	−0.0948	1	0.0029	−0.1010	−0.0887	1.0000
D-m	0.0112	1	0.0029	0.0051	0.0174	1.0000
AB	−0.0314	1	0.0035	−0.0389	−0.0239	1.0000
AC	0.0095	1	0.0035	0.0020	0.0170	1.0000
AD	0.0001	1	0.0035	−0.0074	0.0076	1.0000
BC	−0.0040	1	0.0035	−0.0115	0.0035	1.0000
BD	0.0059	1	0.0035	−0.0016	0.0134	1.0000
CD	−0.0015	1	0.0035	−0.0090	0.0060	1.0000
A^2	0.0068	1	0.0027	0.0010	0.0125	1.05
B^2	−0.0027	1	0.0027	−0.0085	0.0030	1.05
C^2	0.0260	1	0.0027	0.0203	0.0318	1.05
D^2	0.0000	1	0.0027	−0.0057	0.0058	1.05

Table 4 Analysis of variance (ANOVA) for response surface model of quadratic

Source	Sum of Squares	df	Mean Square	F value	p value
Model	0.7629	14	0.0545	273.31	< 0.0001
A-T	0.3937	1	0.3937	1974.73	< 0.0001
B-P	0.1118	1	0.1118	560.70	< 0.0001
C-Camin	0.2158	1	0.2158	1082.54	< 0.0001
D-m	0.0030	1	0.0030	15.23	0.0014
AB	0.0158	1	0.0158	78.99	< 0.0001
AC	0.0014	1	0.0014	7.24	0.0168
AD	2.500E-07	1	2.500E-07	0.0013	0.9722
BC	0.0003	1	0.0003	1.28	0.2750
BD	0.0006	1	0.0006	2.77	0.1168
CD	0.0000	1	0.0000	0.1806	0.6769
A^2	0.0013	1	0.0013	6.31	0.0240
B^2	0.0002	1	0.0002	1.02	0.3275
C^2	0.0186	1	0.0186	93.14	< 0.0001
D^2	1.190E-08	1	1.190E-08	0.0001	0.9939
Residual	0.0030	15	0.0002		
Lack of Fit	0.0026	10	0.0003	3.15	0.1085
Pure Error	0.0004	5	0.0001		
Cor Total	0.7659	29			

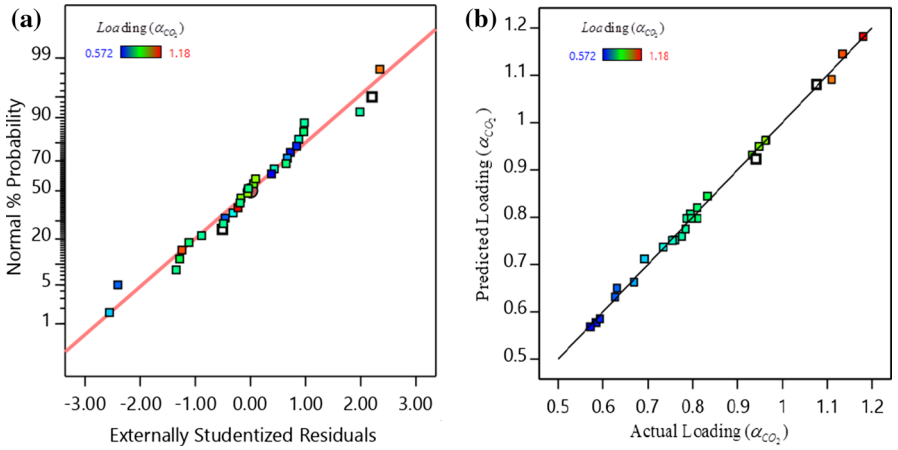

Fig. 3 **a** Normal graph based on standard residuals, and **b** graph of predicted vs. Experimental (Actual) values of CO_2 removal efficiency

$$\begin{aligned} CO_2 Loading =& 1.34474 - 8.775 \times 10^{-3} T + 0.135157P \\ & - 0.204491 C_{TEA} + 0.025 m_{AC} - 2.004 \times 10^{-3} T \\ & \times P + 7.21 \times 10^{-4} T \times C_{TEA} - 7.92 \times 10^{-4} T \times m_{AC} \\ & - 1.194 \times 10^{-3} P \times C_{TEA} + 0.020278 P \times m_{AC} \\ & - 0.012500 C_{TEA} \times m_{AC} + 7 \times 10^{-5} T^2 - 1.116 \\ & \times 10^{-3} P^2 + 0.011662 C_{TEA}^2 + 0.010648 m_{AC}^2 \end{aligned} \quad (15)$$

The normal plot of residuals is shown in Fig. 3a. This diagram depicts how the errors are distributed. The discrepancy between the actual and expected values of

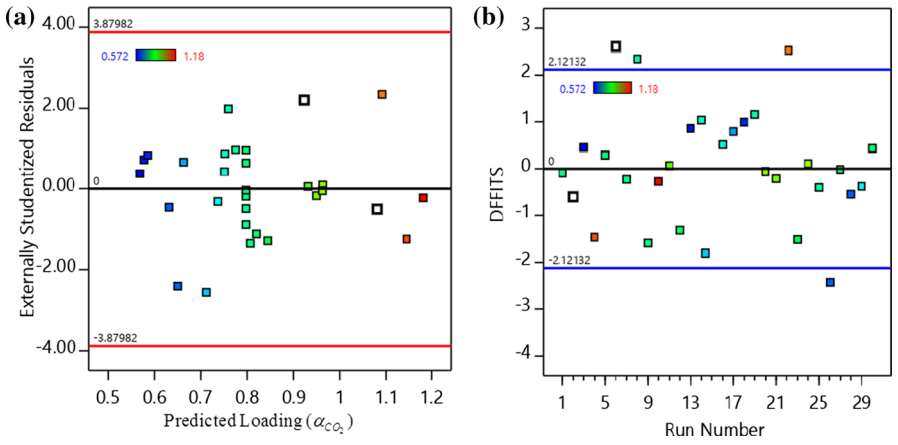

Fig. 4 **a** Externally studentized residuals, and externally studentized residuals vs **b** Number of run

the responses by the model is called an error [45]. Figure 3b shows the correlation between the actual and predicted values, which, as it turns out, are close to each other, and there is a good correlation between the results. The proper distribution of errors is defined by a proper and normal distribution of points along a straight line. Figure 4a shows the residual versus expected answer as a random

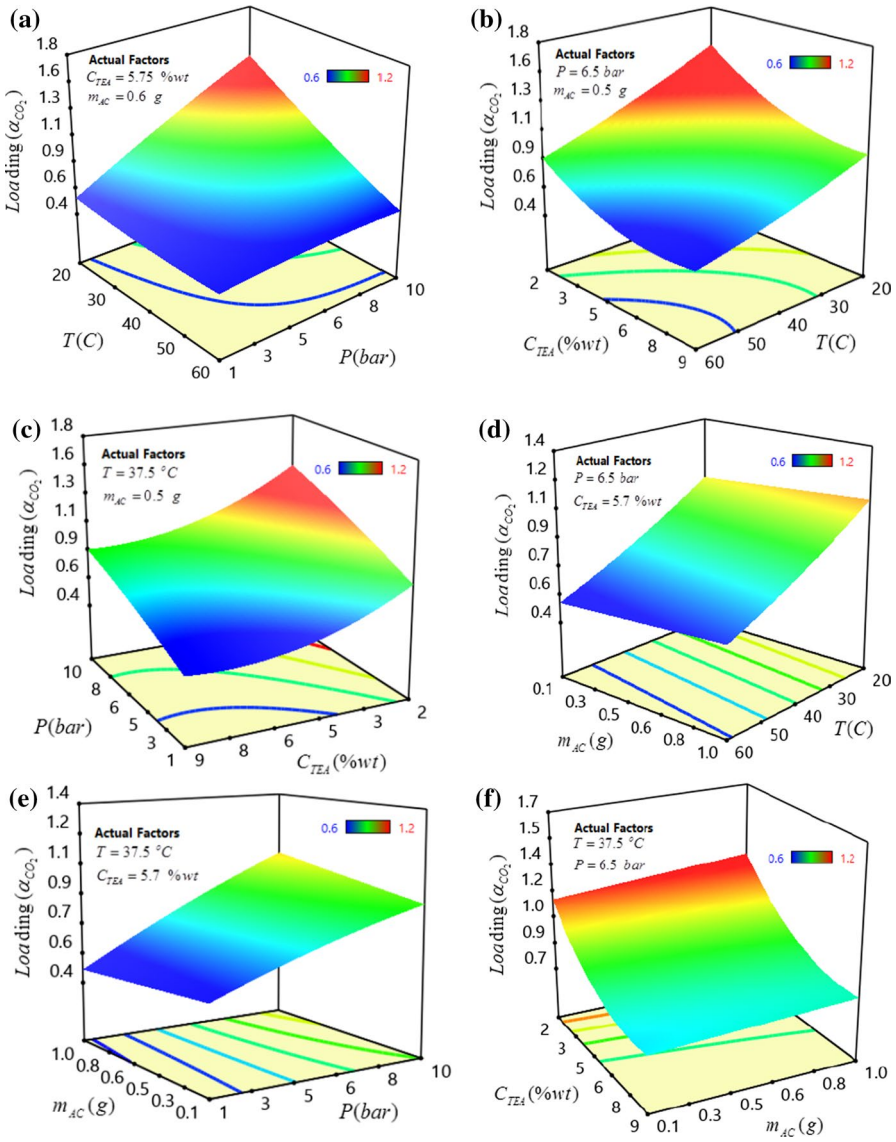

Fig. 5 3D plot response surface of CO_2 loading **a** interaction of T*P on Co_2 loading; **b** interaction of wt% C_{TEA} * T on Co_2 loading; **c** interaction of P* wt% C_{TEA} on Co_2 loading; **d** interaction of m_{AC} * T on Co_2 loading; **e** interaction of m_{AC} * P on Co_2 loading; **f** interaction wt% C_{TEA} * m_{AC} on Co_2 loading

plot. As can be observed, the model did not violate of the constant or independence variance assumption [45]. As shown in Fig. 4d, DFFITS is an impact measurement dependent on the difference in fits in each expected value that occurs when a run is removed.

Analysis of response surface

Response functions for two parameters are shown in these graphs, while all other parameters at the response levels remain constant (Fig. 5). This knowledge helps to understand the direction and interaction impact of each variable [11]. Figure 5 depicts the effects of the interaction between the two variables on the CO_2 loading by the adsorbent. As shown from the graphs, the increase in pressure, decrease temperature, and concentration have increased the CO_2 loading. Increasing the amount of activated carbon has generally had a positive effect on carbon dioxide emissions.

Investigating the effect of operational parameters

Effect of mesh size

Crushing granular activated carbon and running it through a mesh strainer produces adsorbent particle sizes of 200, 300, 500, and 800 µm. The adsorption capacity decreases with increasing particle size, as demonstrated in Fig. 6, since the contact surface reduces with increasing adsorbent particle size. Furthermore, because the adsorbent surface is increasingly exposed to the gas as the particle size is reduced, the mass transfer rate and adsorption intensity rise. The particle size was mixed 200 µm.

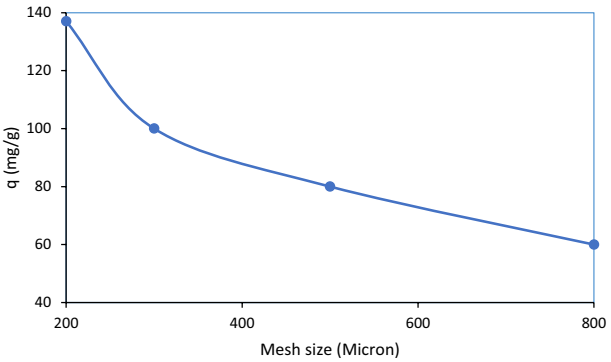

Fig. 6 Effect of mesh size of AC on CO_2 absorption capacity at 40 °C and pressure of 6.5 bar

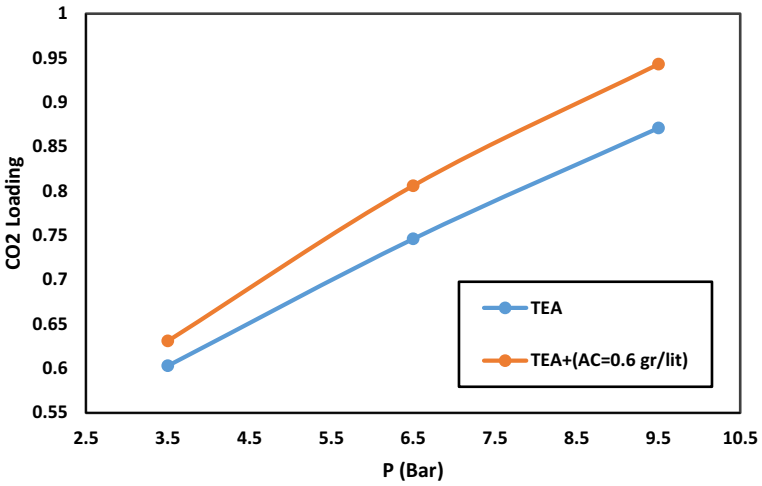

Fig. 7 Effect of pressure on CO_2 loading in TEA solvent in the presence and absence of activated carbon at 313 K and a concentration of 5.5 wt%

Effect of pressure

Figure 7 shows the effect of pressure on CO_2 loading for TEA solvent in the presence and absence of activated carbon particles. Operating conditions at 313 K, TEA concentration, 5.5 wt% at pressures of 3.5, 6.5, and 9.5 bar, and the amount of activated carbon is 0.6 g/L. According to the figure, CO_2 loading increases with increasing pressure, and adding activated carbon particles to the base solvent has a positive effect on the amount of adsorption. The difference between the amount of loading at higher pressures in the presence of activated carbon and its absence is greater than the difference at low pressures, which shows a higher CO_2 loading at high pressures since activated carbon is a physical surface adsorbent. The CO_2 loading is increased by increasing the initial pressure from 3.5 to 9.5 bar [7, 46]. That is due to the higher physical solubility of carbon dioxide in amine solutions, which leads to a chemical equilibrium reaction to the right [Eqs. (12) and (13)]. Therefore, the absorption of this gas increased with amine solutions [7].

Effect of temperature

Temperature programmed analysis was carried out for the samples with an affinity for CO_2 sorption. To evaluate the effect of temperature on CO_2 loading, three TEA solvents with the same conditions of 5.5 wt% of this solvent and 6.5 bar pressure at 293, 313, and 333 K were tested with and without activated carbon. Figure 8 shows the loading of CO_2 against temperature. As shown in Fig. 3, with increasing temperature, CO_2 loads decreases. Also, by adding activated carbon particles to the base solvent, CO_2 loading at different temperatures increases. It can be seen that for TEA + AC the CO_2 is removed as temperature increases at 293 k [7]. Moreover, as

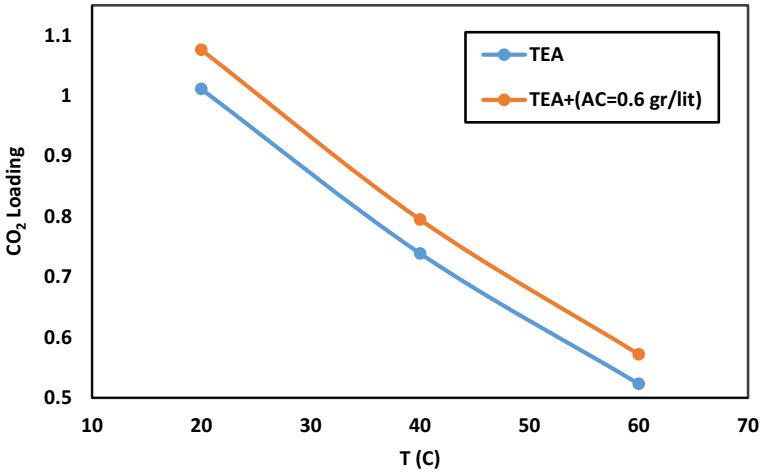

Fig. 8 Effect of temperature on CO_2 loading in TEA solvent in the presence and absence of activated carbon at a pressure of 6.5 bar and a concentration of 5.5% by weight

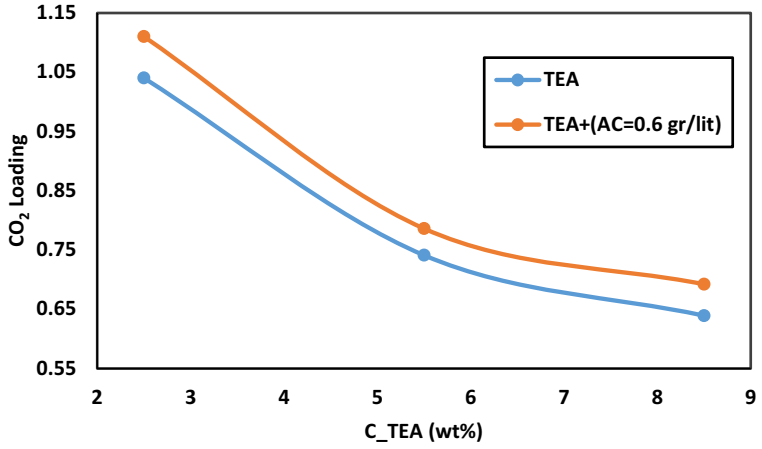

Fig. 9 Effect of TEA solvent concentration on CO_2 loading in the presence and absence of activated carbon at 313 K and a pressure of 6.5 bar

shown in Fig. 7, increased in temperature, CO_2 loading decreased [7]. The physical solubility of this gas in amine solutions decreases with increasing temperature and an exothermic process.

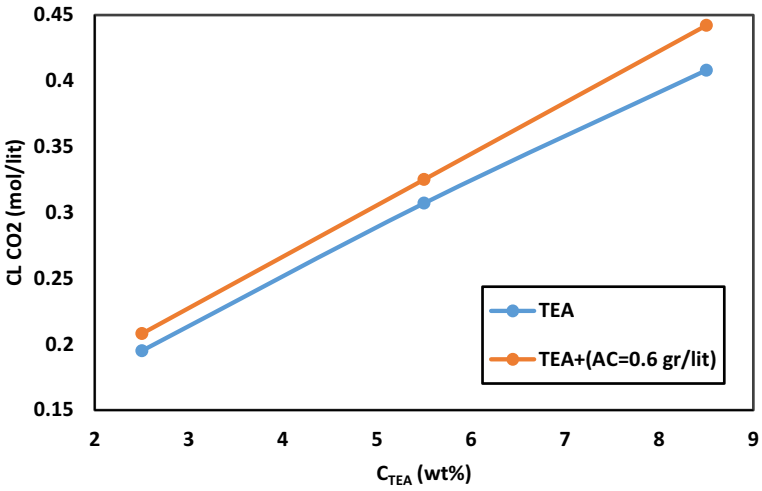

Fig. 10 Effect of TEA solvent concentration on the amount of CO_2 absorbed in the presence and absence of activated carbon at 313 K and a pressure of 6.5 bar

Effect of concentration

To determine the effect of TEA concentration, the loading and the amount of CO_2 adsorbed concentration in three TEA solvents with different concentrations under the same conditions with and without activated carbon particles were measured. As shown in Figs. 9 and 10, CO_2 loading and the amount of CO_2 absorbed in the TEA solvent with activated carbon at all three concentrations

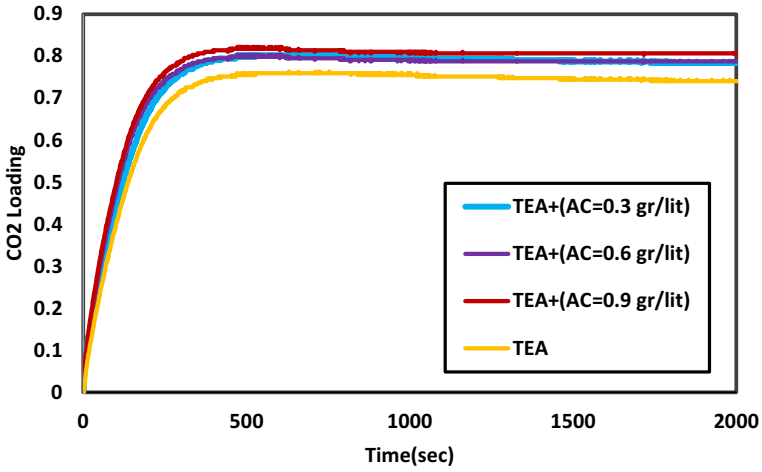

Fig. 11 CO_2 loading in TEA solvent in the presence and absence of activated carbon at 313 K, pressure 6.5 bar and concentration 5.5 wt%

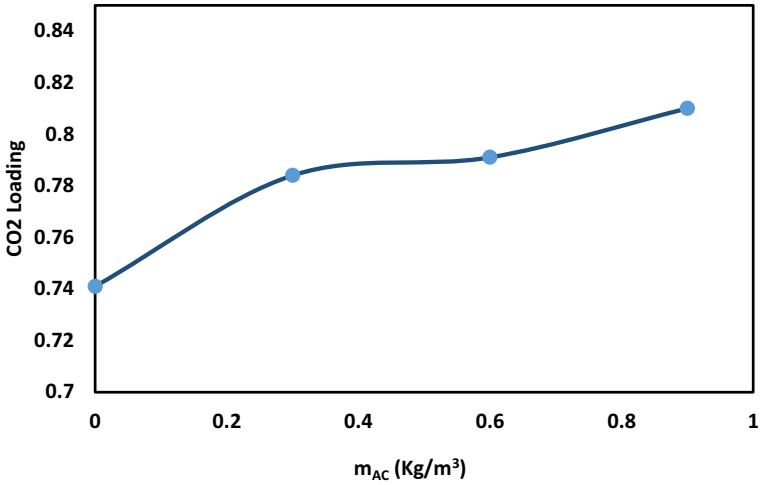

Fig. 12 Effect of activated carbon on CO_2 loading in TEA solvent at 313 K, pressure 6.5 bar and concentration of 5.5 wt%

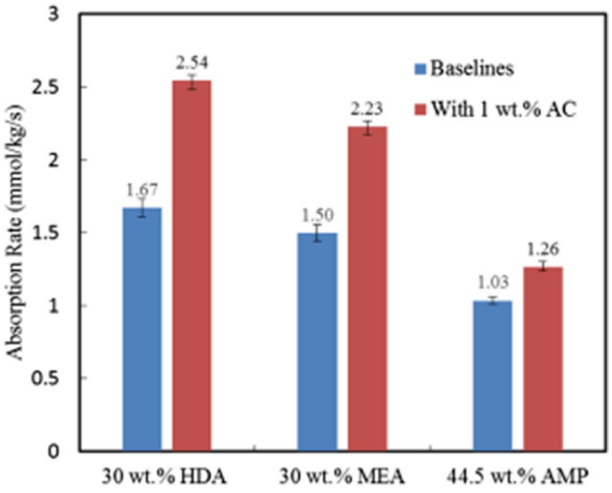

Fig. 13 The effect of adding activated carbon to different amines [19]

tested are higher than the base TEA solvent. Moreover, as shown in Fig. 8, with increase in concentration of amine, CO_2 loading decreased [7]. The higher the concentration of amine solutions, the equilibrium reaction (Eq. 12) shifts to the right according to the theory of Le Chatelier [7]. As the weight percentage of the amine TEA increases, as more ions of the adsorbent are exposing to CO_2, the absorption rate in these solutions increases both in the presence and absence of activated carbon particles.

Effect of activated carbon

Figure 11 shows the effect of activated carbon amount on the CO_2 loading in this solvent with 5.5 wt% at 313 K and a pressure of 6.5 bar. The amounts of activated carbon particles in this solvent were 0.3, 0.6, and 0.9 kg/m^3. According to the diagrams, the addition of activated carbon particles to the base solvent had a positive effect on CO_2 loading. Also, adding the amount of activated carbon from 0.3 to 0.9 kg/m^3, the number of loading and the amount of CO_2 absorbed increase. It can be found that active carbon significantly increases CO_2 loading into the TEA solution. Figure 12 shows the CO_2 loading diagram as a function of the amount of activated carbon, which shows that the activated carbon particles improve the amount of absorption in this range of temperature and pressure. Figure 13 shows the rate of CO_2 uptake by MEA, HDA, and AMP solvents and the effect of adding activated carbon to them in micro-dimensions. As can be seen, activated carbon particles increased the absorption rate for HDA, MEA, and AMP solvents by 52%, 49%, and 22%, respectively [19]. The result of a study showed that the addition of solid particles to chemical solvents effectively enhances CO_2 mass transfer. Experiments show that activated carbon is the most effective particle used. Solvent selection is a significant factor in the effect of solid particles on adsorption performance [19].

Investigating the effect of parameters with RSM

Figures 13a and b show the effects of two parameters and simultaneously on the CO_2 uptake process in a three-dimensional diagram. Figure 14a shows the effects of temperature and pressure on CO_2 loading at TEA concentration and the amount of fixed activated carbon. It is clear that temperature has a negative effect, and pressure has a positive effect on absorption. Figure 14b a three-dimensional diagram of the effects of TEA concentration and the amount of adsorbent activated carbon simultaneously

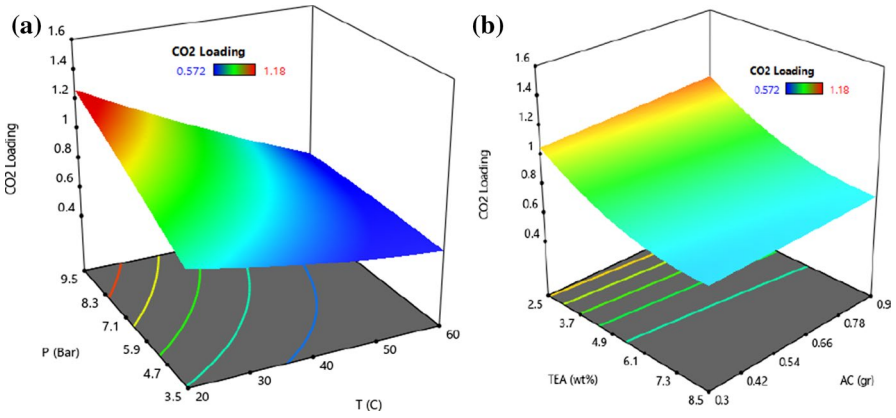

Fig. 14 CO_2 loading in TEA solvent in presence of activated carbon **a** in terms of temperature and pressure, **b** TEA and activated carbon

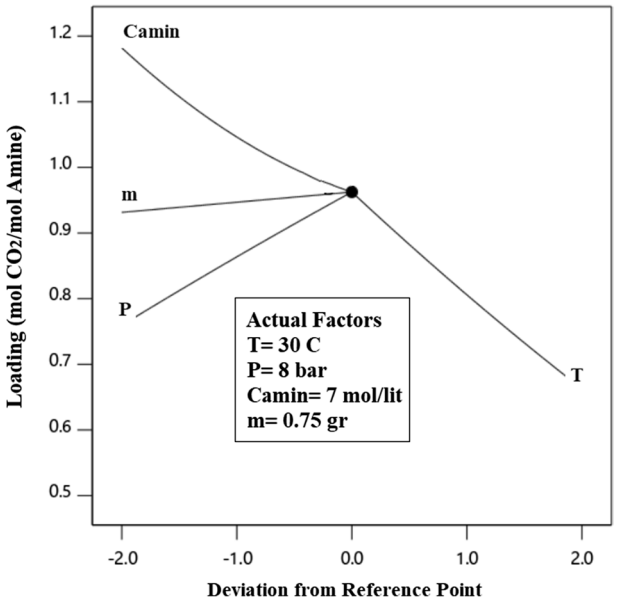

Fig. 15 operating conditions in the optimum point

Table 5 Summary of the design and levels of four independent variables

Name	Goal	Lower Limit	Upper Limit	Lower Weight	Upper Weight	Importance
A:T	is in range	30	50	1	1	3
B:P	is in range	5	8	1	1	3
C:Camin	is in range	4	7	1	1	3
D:m	is in range	0.45	0.75	1	1	3
R	maximize	12.73	32.61	1	1	5
loading(molCo2/molamin)	maximize	0.572	1.18	1	1	5
C_{CO2}	maximize	0.208	0.506	1	1	5

at constant temperature and pressure. Increasing the amount of activated carbon has a positive effect and increases the amount of absorption and CO_2 loading.

Optimization

The numerical optimization portion of Design-Expert software was used to carry out the optimization process. The second-order polynomial model for the answer was used to evaluate the specific optimal conditions in this study [45]. To achieve optimal performance for a set of conditions, each parameter for optimization was used in the range, max, minimum, goal, and none (for answers). In the numerical optimization

section, temperature, pressure, TEA concentration, and activated carbon were selected to reduce process costs and lower energy demand. The optimal conditions based on the desirability function indicate that values of temperature, pressure, amine concentration, and active carbon were obtained 303 K, 8.00 bar, 7.00 M, 0.75 g, and 25.99%, respectively. The desirability index was obtained at 0.732 (Fig. 15). In these conditions, it was estimated equal to 0.961, 0.504 wt%, and 25.962%, respectively. To evaluate the adsorbent's behavior on the absorption of CO_2 for four factors, temperature, concentration, pressure, and adsorbent upper and lower levels are shown in Table 5.

Conclusion

This study aimed to investigate CO_2 uptake using the chemical solvent amine of H_2O-TEA-CO_2 in presence of carbon particles. Increasing the amount of activated carbon has a positive effect and increases the amount of absorption. The activated carbon particles improve the amount of absorption in this range of temperature and pressure. The amount of loading and the amount of CO_2 absorbed in the TEA solvent in the presence of activated carbon at all three concentrations tested are higher than the base TEA solvent. The result showed that the addition of solid particles to chemical solvents effectively enhances CO_2 loading. The CO_2 loading is increased by increasing the initial pressure from 3.5 to 9.5 bar. That is due to the higher physical solubility of carbon dioxide in amine solutions, which leads to a chemical equilibrium reaction. Therefore, the absorption of CO_2 increased with amine solutions.

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