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Removal of CO_2 in a multistage fluidized bed reactor by amine impregnated activated carbon: optimization using response surface methodology

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Abstract Carbon dioxide (CO_2) is the major component of greenhouse gas. Increase in concentration of CO_2 in the atmosphere leads to global warming. To remove the CO_2 from waste flue gas a four-stage counter-current multistage fluidized bed adsorber was developed and operated in continuous bubbling fluidization regime for the two-phase system. This paper describes the optimum condition for CO_2 removal efficiency in a multistage fluidized bed reactor using amine impregnated activated carbon. Response surface methodology with central composite design was used to determine the effect of three variables on the response. The variables are inlet concentration of CO_2 in ppm (ranging from 3000 to 20,000), impregnation ratio of monoethanol amine (ranging from 0.2 to 0.6) and weir height in mm (20–60). The response was CO_2 removal efficiency. The factor which was most influential has been identified from the analysis of variance. The optimum CO_2 removal efficiency for the amine impregnated activated carbon (MEA-AC) was found to be 95.17%, at initial concentration of CO_2 7312.85 ppm, chemical impregnation ratio of 0.31, and weir height 48.65 mm. From the experiment, the CO_2 removal efficiency was found to be 95.97% at the same operating conditions. The predicted response was found to relevance with experimental data.

Keywords Activated carbon · Response surface methodology · Coconut shell · Impregnation ratio · Multistage fluidized bed · Optimization

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1 Introduction

Now a day's due to rapid industrialization and lots of human activities large amount of greenhouse gases are emitted into the environment. The major contributor for global warming is caused by increase in percentage (%) of CO_2 in the atmosphere. The release of CO_2 mainly comes from burning of fossil fuels i.e. coal, oil and natural gas that leads to increase in CO_2 emissions and as a result of which, CO_2 concentrations in the atmosphere increases. Increase of CO_2 concentration leads to trapping of more heat near the surface of the earth. The main disadvantage is the collapse of the ecosystem which lead to more draughts, floods and other extreme weather. To overcome these phenomena CO_2 capture technologies, like absorption, adsorption, cryogenics, and membranes separation technology have been investigated (White et al. 2003; Aaron and Tsouris 2005). The most developed technology is the amine-based absorption process (Bai and Yeh 1997; Yeh and Bai 1999; Rao and Rubin 2002). The major disadvantages associated with this process is corrosion of the process equipment (Hsu et al. 2010) and also this process is energy intensive. Due to serious drawbacks of this process, alternative energy-efficient separation techniques (Arenillas et al. 2005; Gray et al. 2004a, b, 2005) was developed. By taking into the above consideration adsorption is seems to be the most cost effective techniques. So various researchers have studied the development of adsorbent that is easily regenerated and have sufficient strength for high CO_2 selectivity and adsorption capacities (Xu et al. 2002a, b; Drage et al. 2007). Activated carbons (ACs) have high adsorption capacity, regeneration is easier, and highly hydrophobic nature and low cost and can be easily manufactured (Das et al. 2015; Plaza et al. 2010). From the literature, it has been studied that the CO_2 capture capacity can be increased by chemical impregnation (Alvim-Ferraz and Gaspar 2005; Lach et al. 2006; Adamski et al. 2007; Bowker et al. 2007; El-Molla et al. 2007; Xu et al. 2002a, b; Gray et al. 2004a, b; Przepiórski et al. 2004; Das et al. 2016a, b, 2017; Das and Meikap 2018, 2019) i.e. by incorporation of amine functional group.

In our present work, green coconut shell based AC has been prepared because it is considered superior to those obtained from other sources mainly due to small macrospores structure which renders it more effective for the adsorption of gas/vapour and it has high fixed carbon and low ash content (Das et al. 2015) and it has been impregnated with monoethanol amine solution (MEA) for removal of CO_2 in a multistage fluidized bed reactor. MEA-AC shows high % removal of CO_2 because of formation of primary zwitterions in reaction chemistry with CO_2 which was more stable due to inductive effect (Das and Meikap 2019). Multistage fluidized bed reactor with down comer is the most suitable air pollution control equipment for the removal of gaseous pollutants from the industrial flue gas (Mohanty et al. 2008, 2010; Roy et al. 2009; Das et al. 2016a, b, 2017; Das and Meikap 2017, 2018, 2019).

Limited study has been carried out on optimization for the CO_2 removal efficiency (%) in a multi-stage fluidized bed reactor by amine impregnated AC using RSM approach. The influence of operating parameters, such as inlet concentration of CO_2, impregnation ratio of the adsorbents and weir height were investigated in fluidized bed reactor and for process optimization. Statistical experimental design methods have been used. To understand the interaction among the parameter and to build statistical model, the experimental design technique is a very useful tool and it describes the condition under which the process parameters have been optimized (Alam et al. 2007). Among different design methods, the most suitable method is RSM. The main advantage is that RSM based on CCD helps for optimization of the effective parameter and the number of experiments were minimum. It is suitable for fitting a quadratic surface and steps are development of experimental design matrix, building of model and find the optimum region that satisfies the operating specifications (Montgomery 2001). In this paper, optimization framework with surface response methodology is developed to minimize the cost of CO_2 removal for the amine-based adsorbent in multistage fluidized bed reactor.

2 Experimental

2.1 Raw material

In the present experiment, the raw material was green coconut shell. It was collected from nearby local market of IIT Kharagpur, India., followed by washing with normal tap water so that all the dust and adhere impurities were to be removed and then cut into small pieces then dried in sun light for 20–25 days till it completely dry. The dried materials were put in an oven for 48 h at 105 °C for removal of moisture. After oven dried the shells were grounded by locally made grinder and then it was sieved to a size 512 µm.

2.2 Preparation of activated carbon (AC)

The powder precursor was chemical activated with Zinc chloride ($ZnCl_2$). 1 kg of powder material was well mixed with 1 kg of Zinc chloride ($ZnCl_2$) solution in the impregnation ratio (activating agent/precursor) 1:1. Then the impregnated sample was kept for 24 h for proper soaking of chemicals onto the surface of the precursor. The resulting mixture was kept in an air oven and dried for 36 h at 105 °C. The chemical impregnated samples were put inside the muffle furnace by placing in a box made up of stainless steel and heated (10 °C/min) up to the final carbonization temperature of 650 °C under 120 mL/min nitrogen gas flow rate at STP. Samples were held at 650 °C for 1 h. Then it was cooled down under nitrogen gas. The final carbonized samples were washed with 0.5 N HCl, then with hot water and finally washed with cold distilled water for removal of mineral matters and residual organic. Finally the prepared sample was then dried at 105 °C in an air oven till it was completely dry.

2.3 Preparation of amine impregnated activated carbon (MEA-AC)

Twenty sets of dried carbonized powder precursor samples were impregnated with monoethanol amine solution (MEA) at different impregnated ratio (0.2, 0.3, 0.4, 0.5, and 0.6) and kept in an air tight container for further experiment.

2.4 Characterization of adsorbent

The adsorbent used for removal of CO_2 in our experimental set up was monoethanolamine impregnated AC. The adsorbent was characterized by Proximate and Ultimate Analysis, Thermo Gravimetric Analysis (TGA), Scanning Electronic Microscope (SEM), Energy-Dispersive X-ray Spectroscopy (EDX), Fourier Transfer Infrared Spectroscopy (FTIR), X-Ray Diffraction (XRD), Accelerated Surface Area and Porosimetry analyzer (ASAP2020).

3 Multivariate experimental design

RSM along with CCD was used to determine the relationship between three operating variables and the response i.e. for removal efficiency of CO_2 in a multistage fluidized bed reactor. CCD was used for second order model. This method is suitable for fitting a quadratic surface and it helps to optimize the effective parameters with a minimum number of experiments, and also to analyze the interaction between the parameters (Azargohar and Dalai 2005). The first step was formation of design matrix. It consists of a 2^n factorial points, $2n$ axial points and n_c center points (six replicates) (Myers 1971; Napier-Munn 2000). The functions of axial points are that it allows rotatability (Box and Hunte 1957). The functions of center points are evaluation of the experimental error and the reproducibility of data (Sahu et al. 2008, Sahu et al. 2009a, b). An empirical model was developed and the response was correlated to the adsorption of CO_2 process variables using a second-degree polynomial equation as given by the following Eq. (1) (Can et al. 2006; Gönen and Aksu 2008).

$$Y = \beta_0 + \sum_{i=1}^{n} \beta_i X_i + \sum_{i=1}^{n} \beta_{ii} X_i^2 + \sum_{i=1}^{n} \sum_{j=i+1}^{n} \beta_{ij} X_i X_j + \varepsilon \quad (1)$$

where Y is the predicted response, β_0 is the constant coefficient, β_i is the linear coefficients, β_{ii} is the interaction coefficients, β_{ij} is the quadratic coefficients and $X_{i,}X_j$ are the coded values of the removal efficiency of CO_2 by MEA-AC in a multistage fluidized bed reactor. ε is the random error. n is the number of factor studied.

For three variables (n), the total number of tests (N) required is 20 (Box and Hunter 1961). It consisting of 8 factorial points, 6 axial points and 6 replicates at the centre points were employed, indicating that altogether 20 experiments were required, as calculated from Eq. (2) (Azargohar and Dalai 2005).

$$N = 2^n + 2n + n_c = 2^3 + (2 \times 3) + 6 = 20 \quad (2)$$

The coded variables for factorial points are lie at $\pm$ 1 and $\pm$ α for the axial points and 0 for the center points.

3.1 Statistical analysis

The Design-Expert software version 7.0.0 was used for regression analysis of experimental data to estimate the statistical parameters.

3.2 Experimental set up and procedure

The schematic diagram of four staged fluidized bed reactor was shown in Fig. 1. The fluidized bed column was consisted of four stages (0.21 m height per stage and 0.095 m internal diameter). Stages were assembled together with flanged joint. In between the stages of the fluidized bed reactor four number of stainless steel made plate (S_1, S_2, S_3, S_4) of 0.002 m thick were used and it was drilled with hole of diameter 0.002 m. A fine weir mesh (100 mesh size) was there on the grid plate to avoid the solids were falling down through the plate, down comers (D_1, D_2, D_3, D_4) of 0.024 m internal diameter and height of 0.265 m and it made up of Perspex cylinder. Each section was provided with down-comers and it was further fitted with a cone of diameter 0.007 m and 0.024 m height at the bottom end so that the up-flow of the gas through the down-comer was reduced to maintain stable operation. The down-comers were further fitted to the gas distributor by some threading arrangement to adjust the weir height as required.

The weir height is considered to be bed height. The material flows from stage to stage through the down-comer. There were provisions for measuring pressure drop. For uniform distribution of the gas to the fluidization column, gas distributor was there at the bottom of the column. Calibrated rotameter was fitted to measure the air flow rate. For storage of the solid coming from the fluidized bed column a conical hopper was attached. A feeding funnel was there at the top of the column to hold the amine impregnated activated carbon particles and it was attached to the screw feeder. Screw feeder was fitted to a motor of 0.25 HP and the speed of the motor was controlled by a variable rheostat. Compressor was used to supply the air as fluidizing gas having capacity 5HP. The solid fed to the first stage of the down-comer from the top of the funnel connected to screw feeder and then through Perspex tube (0.011 m internal diameter). The gas leaving the top stage is passed through 0.14 m diameter cyclone. To collect the fines coming out

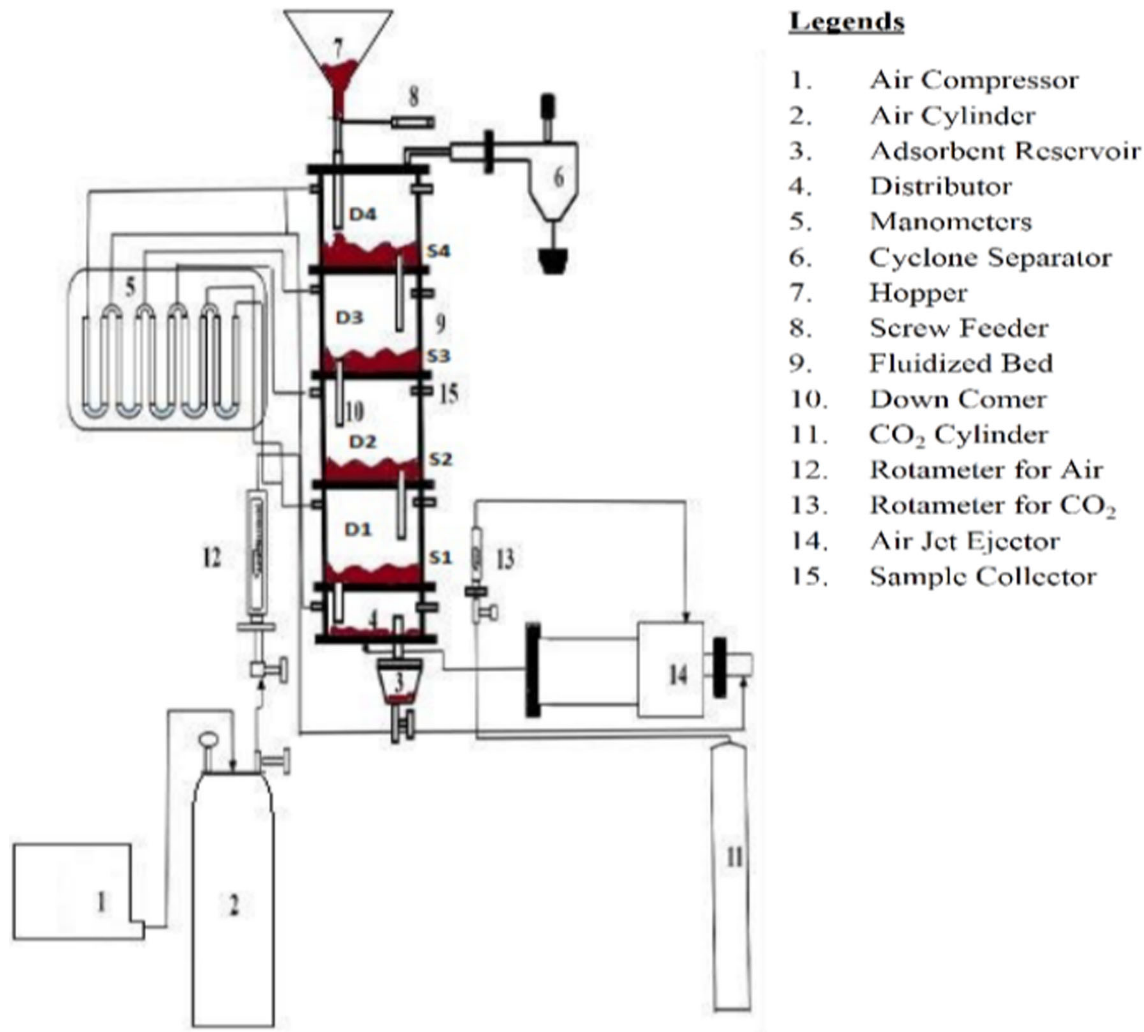

Fig. 1 Schematic diagram of the experimental set-up of a four stage counter-current fluidized bed reactor

from the fluidized bed, a bag is attached to the bottom of the cyclone. There was provision to feed the air-CO_2 mixture at the bottom of the fluidized bed reactor from in the mixing chamber. The air should not be enter into the column. The experiments were conducted by setting the gas velocity of 0.188 m/s corresponding to solid flow rate of 4.12 kg/h. The experiment was conducted at normal room temperature. The experimental variables are considered as chemical impregnation ratio ranging from 0.2 to 0.6, the inlets CO_2 loadings concentration were varied from 3000 to 20,000 ppm and weir height 20 to 60 mm. Since those parameters were important parameters that affects the CO_2 removal efficiency (%) by amine impregnated activated carbon particles in a fluidized bed reactor.

3.3 Sampling and analysis

When all stages of the reactor were identical in their operation and the pressure drops across each stage were almost equal, then it indicated steady and stable operation reactor. At that time samples at the inlet and outlet of the column were drawn with the help of aspirator bottles and the obtained CO_2 gas samples were analyzed by Orsat analysis. The gas samples i.e. concentration of CO_2 in CO_2 + air mixture were analyzed for CO_2 by the "Orsat Analysis" method. Aspirator bottle filled with kerosene; one end of the bottle was fitted below the inlet section of the first stage fluidized bed reactor through a pipe and the other end is connected to the collecting jar. By downward displacement of kerosene CO_2 + air mixture has been collected into the aspirating bottles. Then this air and CO_2 mixture from aspirating bottle was taken inside Orsat apparatus. By noting the level difference of initial and final marking of measuring burette the volumetric percentage of concentration of CO_2 has been found out and then the volumetric concentration of CO_2 was converted to ppm.

3.3.1 *Orsat analysis*

Figure 2 shows the Orsat apparatus. It consists of measuring burette and absorption pipette. Measuring burette was connected to leveling bottle which contains a mixture of potassium dichromate, water, and sodium chloride. Absorption pipette contains potassium hydroxide which absorbs CO_2. Figure 3 shows the aspirator bottle. The aspirator bottle was used to collect and analyze CO_2 gas sample. First the mixture of solution (potassium dichromate, sodium chloride, water) in measuring burette is adjusted as 100 ml using a leveling bottle by opening and closing the inlet valve. The potassium hydroxide level in adsorption pipette was recorded, and then one end of aspirator bottle was connected to the capillary tube and the other end is connected to the leveling bottle that contains kerosene. The valves of aspirator bottle and inlet valve were opened. After lifting the water bottle, the reading in burette decreases as CO_2 enters into the burette simultaneously. When the reading reaches zero, the inlet valve was closed. The absorption pipette valve was opened, and then the leveling bottle is adjusted for 30–50 times till all the CO_2 gas samples are absorbed in the KOH. After that the valve was closed and the final reading was noted. The change in reading gives the volume % of CO_2 absorbed by the KOH solution. Then it was converted to ppm.

The CO_2 removal efficiency (%) has been calculated for each experimental run by Eq. (3)

$$CO_2\ \textit{removal efficiency}\ (\%) = \frac{CO_{2\ \mathrm{inlet}} - CO_{2\ \mathrm{outlet}}}{CO_{2\ \mathrm{inlet}}} \times 100 \tag{3}$$

$$\eta_{CO_2} = \frac{C_{i+1} - C_i}{C_{i+1}} \times 100 \tag{4}$$

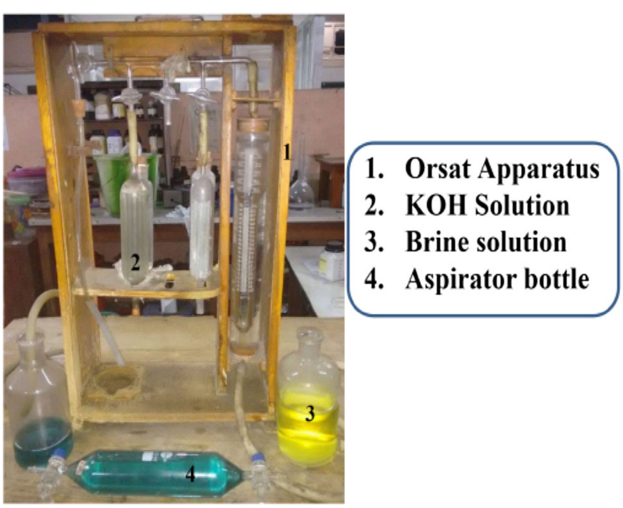

Fig. 2 Orsat apparatus

Fig. 3 Aspirator bottle

where C_i and C_{i+1} are outlet and inlet CO_2 concentrations in gas.

4 Results and discussions

4.1 Development of regression model equation

Design expert software has been used for analysis of experimental data by development of regression model equation. Central composite design (CCD) was used to develop correlation between the CO_2 removal efficiency (%) and the independent variables. The purpose of Response Surface Methodology (RSM) is to analyze the interaction between the parameters and also to optimize the effective parameters with a minimum number of experiments (Azargohar and Dalai 2005). Table 1 shows the relationship between coded and actual value of the variables. The levels and experimental range of independent variables are given in Table 2. The quadratic model was selected as suggested by the software. The design matrix along with response of this experiment was given in Table 3. There are six replicates at the center point. To fit the response function of the CO_2 removal efficiency (%), regression analysis was performed. The final empirical model in terms of coded factors for CO_2 removal efficiency (%) (*Y*) Is given in Eq. (5),

$$Y = 91.69 - 2.84X_1 - 1.53X_2 + 0.98X_3 + 0.79X_1X_2 + 0.57X_1X_3 - 0.26X_2X_3 - 0.94X_1^2 - 1.34X_2^2 + 0.04X_3^2 \tag{5}$$

Table 1 Relationship between coded and actual value of the variables

Code	Actual level of variable
− α	X_{min}
− 1	$[(X_{max} + X_{min})/2] - [(X_{max} - X_{min})/2\beta]$
0	$(X_{max} + X_{min})/2$
+ 1	$[(X_{max} + X_{min})/2] + [(X_{max} - X_{min})/2\beta]$
+ α	X_{max}

X_{max} and X_{min} are maximum and minimum values of X, respectively; β is $2^{n/4}$

In the above correlation, the CO_2 removal efficiency (%) (Y) is the function of inlet concentration of CO_2 (X_1), impregnation ratio (X_2) and weir height (X_3). From their coefficient of correlation, quality of the model was judged.

4.2 Statistical analysis

Table 4 shows the analysis of variance (ANOVA) for CO_2 removal efficiency (%). The model adequacy check was done by seeing to residual plots by approximating model (Box et al. 1978). The studentized residuals measure the number of standard deviations separating the actual and predicted values. The normal probability and studentized residuals plot is shown in Fig. 4. Figure 5 shows the studentized residuals verses predicted CO_2 removal efficiency (%). This plot exhibited a funnel-shaped pattern (Mahalik et al. 2010; Sahu et al. 2009a, b, 2010; Myers and Montgomery 2002) due to the variance of the response depends on the mean level of Y. The actual and the predicted CO_2 removal efficiency (%) are shown in Fig. 6. This indicates that there was no need for transformation of the response variable.

Table 5 shows the statistical parameter obtained from the analysis of variance (ANOVA) for the model for CO_2 removal efficiency (%). The values of R^2 was found to be 0.98, which close to unity and R^2_{adj} was 0.96. It shows that there is a good agreement between the experimental and the predicted values from the model. The predicted R^2 value is 0.81. The standard deviation was 0.77. It shows that the model was better and gives the predicted values that closer to the actual values for the response. F-value 47.07 shows the model was significant. The probability value less than 0.05 would be considered with a significant effect. Table 4 shows that X_1 (initial concentration of CO_2), X_2 (impregnation ratio), X_3 (weir height), X_1X_2 (interaction term), X_1^2, X_2^2 are all significant model terms and X_1X_3 and X_2X_3 were insignificant term. The value of 79.57 for the "Lack of Fit F-value" implies that Lack of Fit is significant relative to the pure error. Experimental values were very close to the predicted values that indicate the developed model was successful in capturing CO_2 in a multistage fluidized bed reactor.

4.3 CO_2 removal efficiency (%) in multistage fluidized bed reactor

Based on the ANOVA results obtained, inlet concentration of CO_2, impregnation ratio of the adsorbent and weir height were found to have significant effects on CO_2 removal efficiency(%). Impregnation ratio and initial concentration of CO_2 imposing the greatest effect on CO_2 removal efficiency (%) in a multistage fluidized bed reactor. Weir height on the other hand imposed moderate effect on the response. The quadratic effects are impregnation ratio and initial concentration and the interaction effect X_1X_2 are significant and X_1X_3, X_2X_3, were considered moderately significant. The response surface graphs of CO_2 removal efficiency (%) are shown in Figs. 7, 8 and 9.

Figure 7 shows the combined effect of impregnation ratio (X_2) and inlet CO_2 concentration (X_1) on CO_2 removal efficiency (%) at constant weir height of 40 mm. A maximum CO_2 removal efficiency was 94.07% and that was determined at constant weir height. When the impregnation ratio of the adsorbent increases the CO_2 removal efficiency (%) was also increases progressively and with increase in inlet concentration of CO_2, the CO_2 removal efficiency (%) decreases because due to an increase in concentration on the surface of amine impregnated activated carbon particle and formation of monolayer which results in decrease of the adsorbent activity (Das et al. 2016a, b; Das and Meikap 2018, 2019).

The combined effect of inlet CO_2 concentration (X_1) and weir height (X_3) on CO_2 removal efficiency (%) at constant impregnation ratio is shown in Fig. 8. In the three dimensional response surfaces, the maximum CO_2 removal efficiency (%) was 94.07% and was determined at constant

Table 2 Experimental range and levels of independent variables

Variables	Symbol	− α	− 1	0	+ 1	+ α
Inlet concentration of CO_2 (ppm)	X_1	3000	7250	11,500	15,750	20,000
Impregnation ratio (IR) (g/g)	X_2	0.2	0.3	0.4	0.5	0.6
Weir height (mm)	X_3	20	30	40	50	60

Table 3 Experimental design matrix and results

Run	Coded level of variables			Actual level of variables			CO_2 removal efficiency (%)
	X_1	X_2	X_3	X_1 (ppm)	X_2 (wt%)	X_3 (mm)	
1	− 1	− 1	− 1	7250	0.3	30	93.96
2	+ 1	− 1	− 1	15,750	0.3	30	86.32
3	− 1	+ 1	− 1	7250	0.5	30	89.95
4	+ 1	+ 1	− 1	15,750	0.5	30	85.72
5	− 1	− 1	+ 1	7250	0.3	50	94.96
6	+ 1	− 1	+ 1	15,750	0.3	50	89.82
7	− 1	+ 1	+ 1	7250	0.5	50	90.13
8	+ 1	+ 1	+ 1	15,750	0.5	50	87.93
9	− α	0	0	3000	0.4	40	94.07
10	+ α	0	0	20,000	0.4	40	80.97
11	0	− α	0	11,500	0.2	40	89.22
12	0	+ α	0	11,500	0.6	40	82.63
13	0	− 0	− α	11,500	0.4	20	89.27
14	0	0	+ α	11,500	0.4	60	93.63
15	0	0	0	11,500	0.4	40	91.66
16	0	0	0	11,500	0.4	40	91.56
17	0	0	0	11,500	0.4	40	91.63
18	0	0	0	11,500	0.4	40	91.58
19	0	0	0	11,500	0.4	40	91.32
20	0	0	0	11,500	0.4	40	91.59

Table 4 Analysis of variance (ANOVA) for response surface quadratic model for CO_2 removal efficiency (%)

Source	Sum of squares	Degree of freedom	Mean square	F value	Prob > F	Remarks
Model	251.68	9	27.96	47.07	< 0.0001	Significant
X_1	128.88	1	128.88	216.93	< 0.0001	Significant
X_2	37.55	1	37.55	63.2	< 0.0001	Significant
X_3	15.23	1	15.23	25.63	0.0005	Significant
X_1X_2	5.04	1	5.04	8.48	0.0155	Significant
X_1X_3	2.57	1	2.57	4.32	0.0644	
X_2X_3	0.56	1	0.56	0.94	0.3559	
X_1^2	22.32	1	22.32	37.58	0.0010	Significant
X_2^2	45.22	1	45.22	76.11	< 0.0001	Significant
X_3^2	0.041	1	0.041	0.068	0.7989	
Residual	5.94	10	0.59			
Lack of fit	5.87	5	1.17	79.57	< 0.0001	Significant
Pure error	0.074	5	0.015			
Cor Total	257.62	19				

impregnation ratio 0.4. From the Fig. 8. It was observed that with increase in weir height the CO_2 removal efficiency (%) increases because with increase in the weir height CO_2 removal efficiency (%) increases due to increase in bed volume resulting in more gas solid interaction. However, the effect of weir height at lower concentration was not as much as observed at higher concentration indicating the presence of less quantity of reactive solids at lower height (Das et al. 2016a, b; Das and Meikap 2018, 2019).

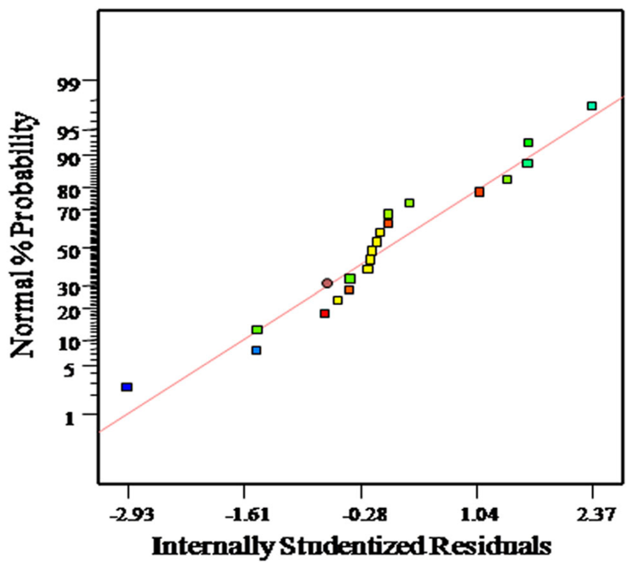

Fig. 4 The studentized residuals and normal % probability plot of CO_2 removal efficiency (%)

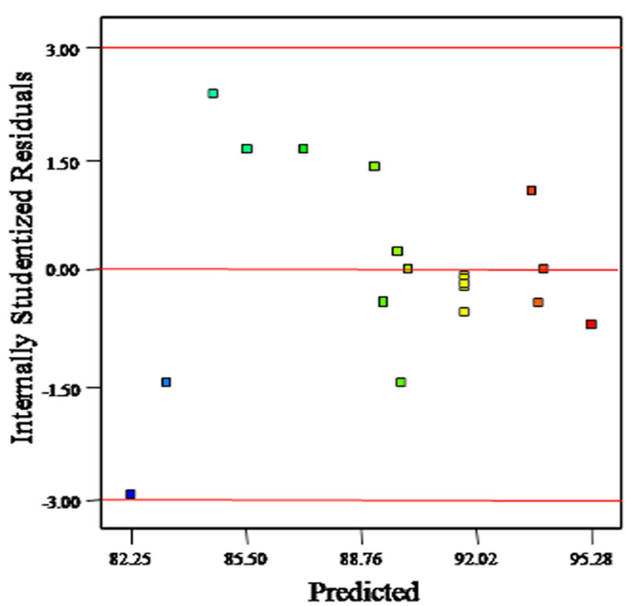

Fig. 5 The predicted CO_2 removal efficiency (%) and studentized residuals plot

Figure 9 shows the three dimensional response surfaces which was constructed to show the most important two variables (impregnation ratio and weir height) on the CO_2 removal efficiency (%) at constant inlet concentration. Maximum CO_2 removal efficiency was 93.63% was determined at constant CO_2 inlet concentration 11,500 ppm. From the Fig. 9 it was shown that with increase in impregnation ratio and weir height, the CO_2 removal efficiency (%) increases (Das and Meikap 2018, 2019).

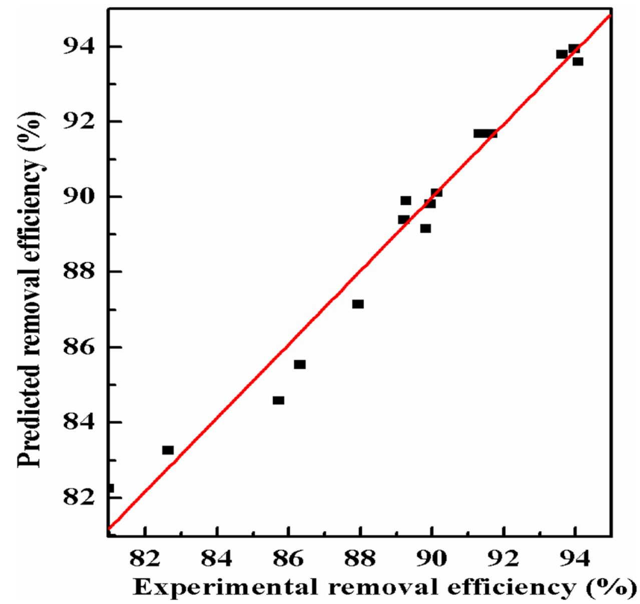

Fig. 6 The actual and predicted plot of CO_2 removal efficiency (%)

Table 5 Statistical parameter obtained from the analysis of variance (ANOVA) for the model for CO_2 removal efficiency (%)

SD	0.77
Mean	89.9
C.V.(%)	0.86
PRESS	48.06
R^2	0.98
Adjusted R^2	0.96
Predicted R^2	0.81
Adeq precision	23.92

4.4 Optimization by response surface modeling

To maximize the CO_2 removal efficiency (%), the optimum process parameters in a multi stage fluidized bed reactor and development of mathematical model equation have been found out. The quadratic model equation was optimized to maximize the CO_2 removal efficiency (%) within the experimental range studied. Optimal processing conditions from numerical optimization were given in Table 6. The contour plot was shown in Fig. 10 and it shows the optimum region on the inlet concentration of CO_2 and impregnation ratio for the CO_2 removal efficiency (%). Figure 11 shows the 3D plot showing the optimum region for the combined effect of inlet concentration of CO_2 and impregnation ratio for the CO_2 removal efficiency (%). The optimum production conditions were initial CO_2 concentration 7312.85 ppm, impregnation ratio 0.31 and weir height 48.65 mm and have been determined as optimum levels of the process parameters to achieve the maximum

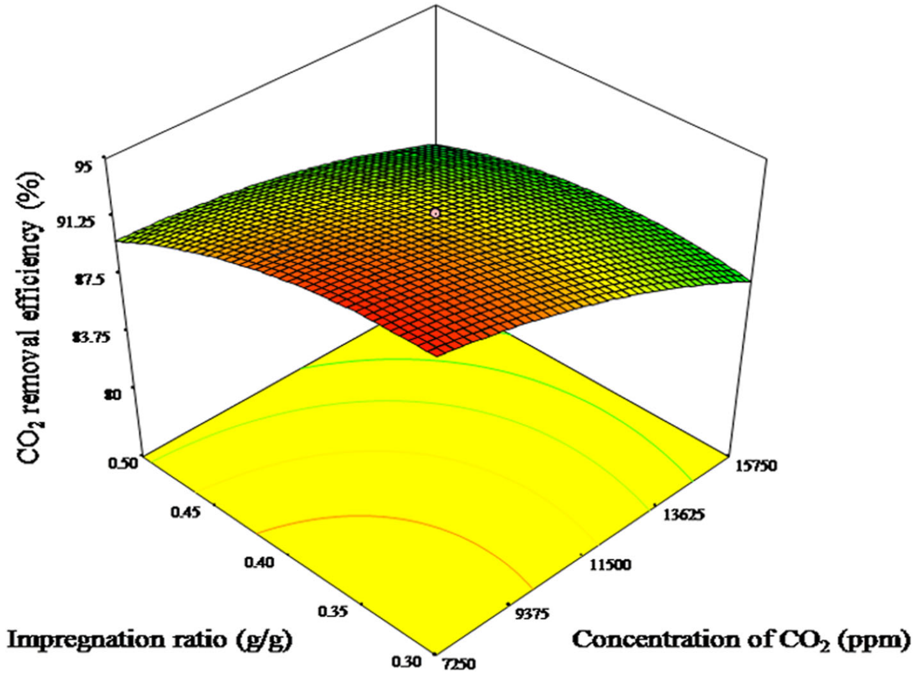

Fig. 7 Combined effect of impregnation ratio and initial concentration of CO_2 on CO_2 removal efficiency (%) at weir height 40 mm

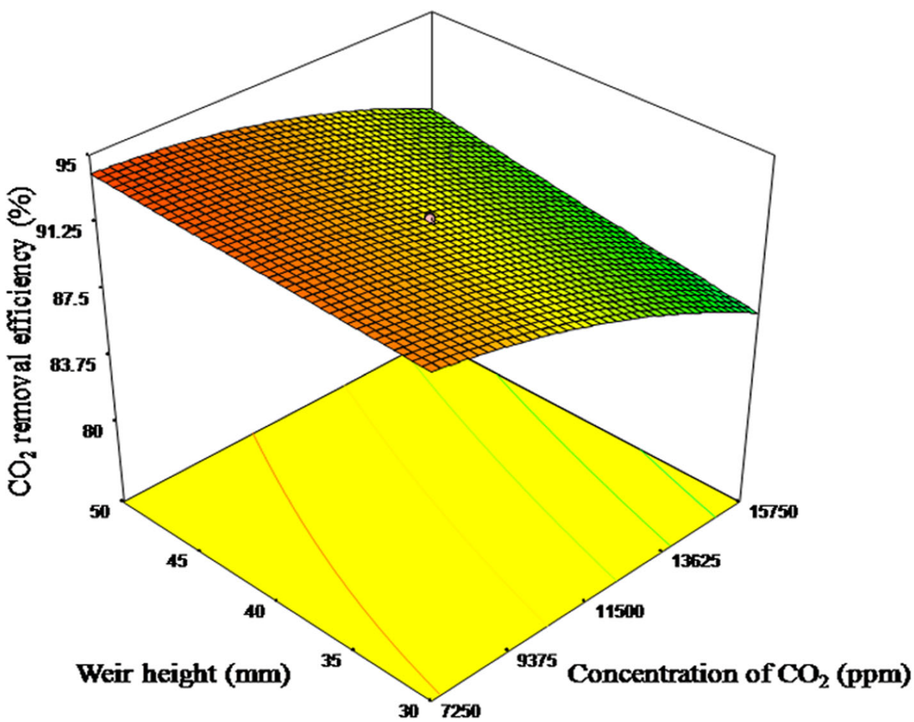

Fig. 8 Combined effect of initial concentration of CO_2 and weir height on CO_2 removal efficiency (%) at impregnation ratio 0.4

CO_2 removal efficiency 95.17%. From the experiment it was found that for the same operating condition the CO_2 removal efficiency was 95.97%. After comparison the experimental and predicted result, it can be seen that the error between the experimental and predicted result was nearly same.

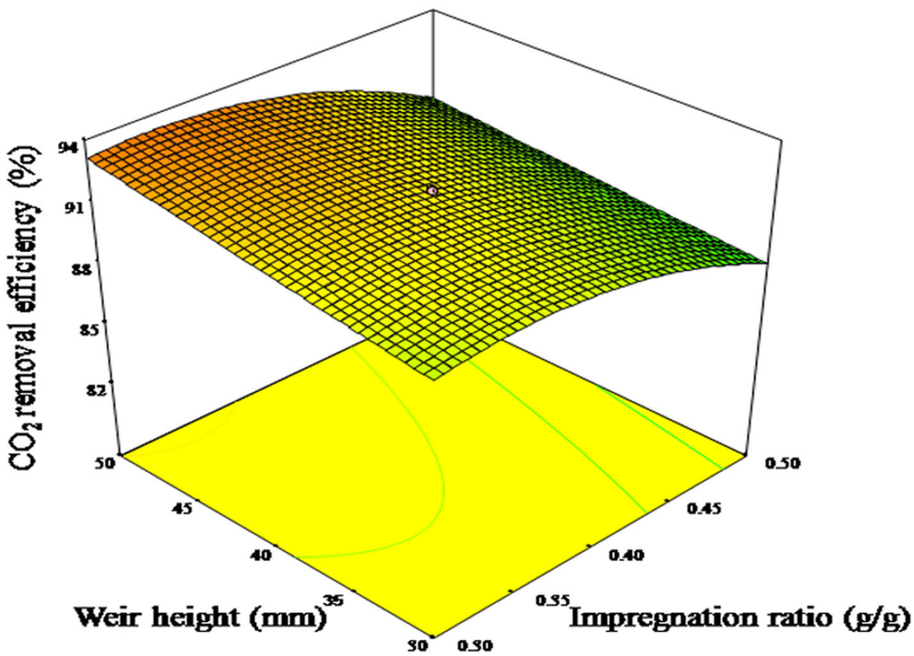

Fig. 9 Combined effect of weir height and impregnation ratio on CO_2 removal efficiency (%) at CO_2 concentration 11,500 ppm

Table 6 Optimal processing conditions from numerical optimization

Parameters	Inlet concentration of CO_2 (ppm)	Impregnation ratio (g/g)	Weir height (mm)	CO_2 removal efficiency (*Y*) (%)	
				Predicted	Experimental
Optimum condition	7312	0.31	48.65	95.17	95.97

5 Characterization of prepared amine impregnated AC under optimum condition

Different characterization techniques like Proximate Analysis, Ultimate Analysis, Accelerated Surface Area and Porosimetry analyzer (ASAP2020), Scanning Electronic Microscope (SEM), Fourier Transfer Infrared Spectroscopy (FTIR) and X-Ray Diffraction (XRD) have been used for analysis of the prepared activated carbon under optimum condition. From the proximate analysis it has been seen that, the carbon content of AC and MEA-AC was very high as compared to raw precursor. From the Ultimate analysis, it has been seen that the nitrogen content of MEA-AC sample under optimum condition was more as compared to activated carbon and the raw precursor (i.e. 7.72%), which results in better adsorbents for adsorption purpose. The results of the proximate and ultimate analysis is shown in Table 7. From the Brunauer–Emmet–Teller (BET) analysis, the surface area of MEA-AC prepared under optimum condition was found to be 572.27 m^2/g. The pore size distribution was determined by using Barrett–Joyner–Halenda (BJH) model and the t plot determines the volume of the micropore and found to be 0.259 cm^3/g. The pore structure parameter of the amine impregnated AC sample under optimum condition is shown in Table 8. Due to amine impregnation the surface area decreases as compared to AC and creates so many of active sites for CO_2 capture. From SEM analysis it has been seen that pores are not clearly visible in case of MEA-AC. The SEM micrograph of MEA-AC under optimum condition is shown in Fig. 12. This signifies the pores are filled with impregnated solvent. The FTIR spectra of MEA-AC under optimum condition is shown in the Fig. 13. From the FTIR analysis it has been seen that, all kinds of functional groups and amine functional groups are present in amine impregnated activated carbon. X-ray Diffraction graph shows the absence of any sharp peaks in amine impregnated AC. That concludes the structure is predominantly amorphous in nature and hence got advantageous property for well-defined adsorbent. The XRD graph of the sample is shown in the Fig. 14.

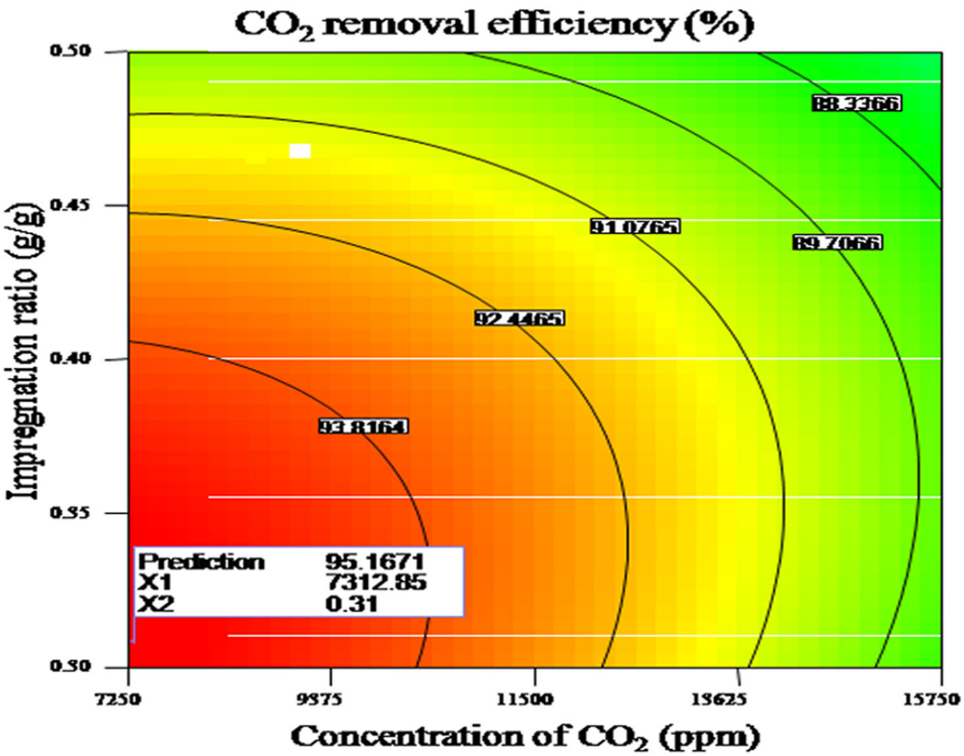

Fig. 10 Optimum region on the inlet concentration of CO_2 and impregnation ratio for the CO_2 removal efficiency (%)

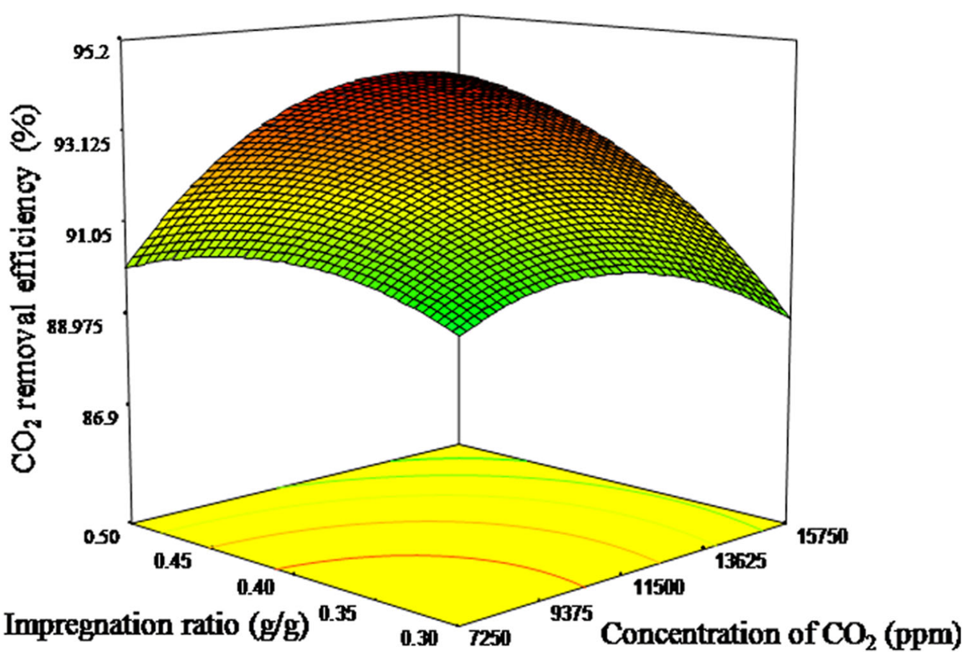

Fig. 11 The 3D plot showing the optimum region for the combined effect of inlet concentration of CO_2 and impregnation ratio for the CO_2 removal efficiency (%)

Table 7 Proximate and ultimate analysis of adsorbents (at optimum condition)

Sample	Proximate analysis				Ultimate analysis				
	Moisture (%)	Volatile matter (%)	Ash (%)	Fixed carbon (%)	C (%)	H (%)	N (%)	O (%)	S (%)
RAW	13.83	44.97	2.56	38.64	46.18	9.41	0.99	33.38	10.04
AC	12.98	7.21	1.90	77.91	69.04	2.96	1.16	26.79	0.05
MEA-AC	10.45	17.42	0.4	71.73	68.14	3.55	7.72	20.32	0.27

Table 8 BET surface area and pore size distribution (at optimum condition)

Samples	S_{BET} (m^2/g)	v_T (cm^3/g)	M.P.V. (cm^3/g)	Avg. pore radius (Å)	Micro pore area (m^2/g)
RAW	59.73	0.05	0	16.85	0
AC	995.79	0.449	0.37	9.0119	921.71
MEA-AC	572.27	0.26	0.21	9.94	492.72

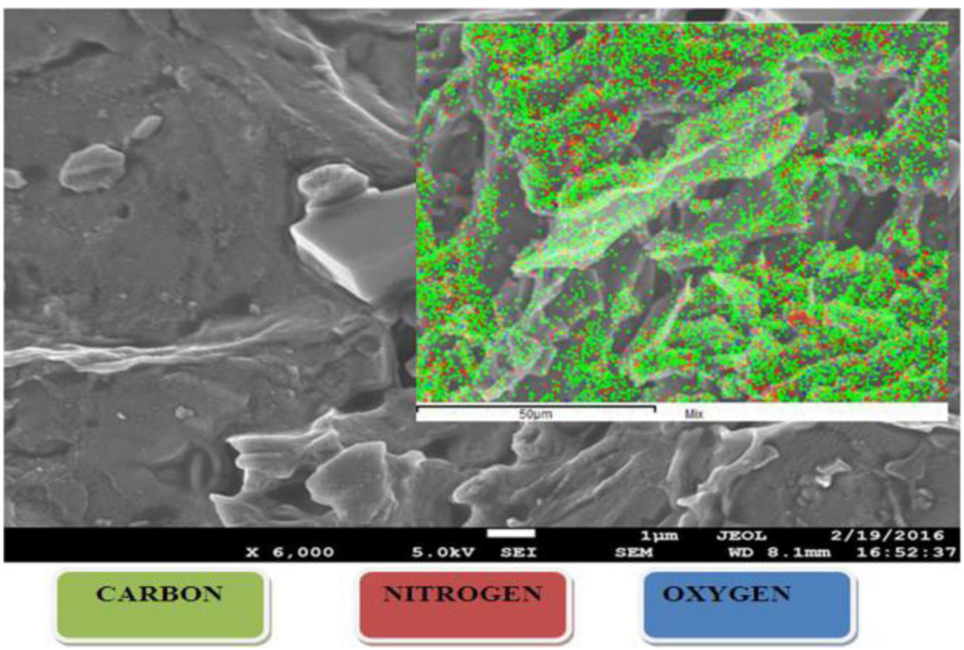

Fig. 12 SEM Analysis of MEA-AC (at optimum condition)

6 Conclusions

In this study, CO_2 was removed in a four stage fluidized bed reactor by amine impregnated activated carbon. The response surface methodology using central composite design used to determine the effect of inlet CO_2 concentration (3000–20,000) ppm, impregnation ratio of adsorbent (0.2–0.6) and weir height (20–60) mm on CO_2 removal efficiency (%). The regression analysis and optimization of variables has been found out by the use of statistical design expert software. A model was developed to correlate the three variables to the response. 3D response surface plot helps to describe the effect of the process variables on the CO_2 removal efficiency (%). From the process optimization it was found that experimental values obtained for CO_2 removal efficiency (%) are found to agree satisfactorily with the model predicted value. The optimum production conditions are initial concentration of CO_2 (7312 ppm), chemical impregnation ratio (0.31) and weir height (48.65 mm) and the optimum removal efficiency was found to be 95.17%. At the same operating condition the CO_2 removal efficiency was found to be 95.97% found from the experiment. The experimental value was found to agree well with that of predicted value.

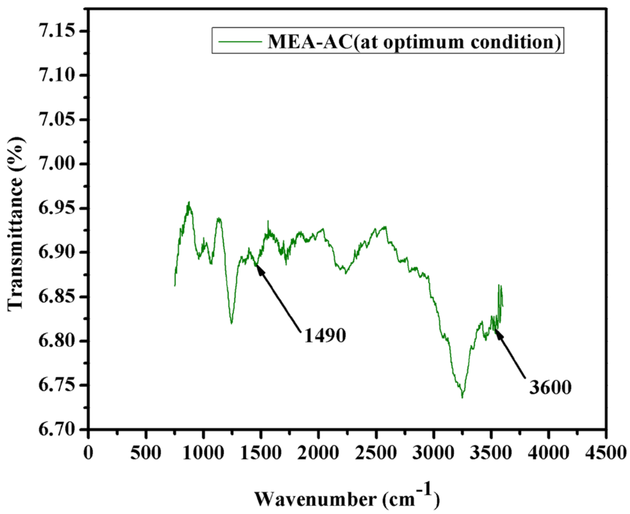

Fig. 13 FTIR Analysis of MEA-AC (at optimum condition)

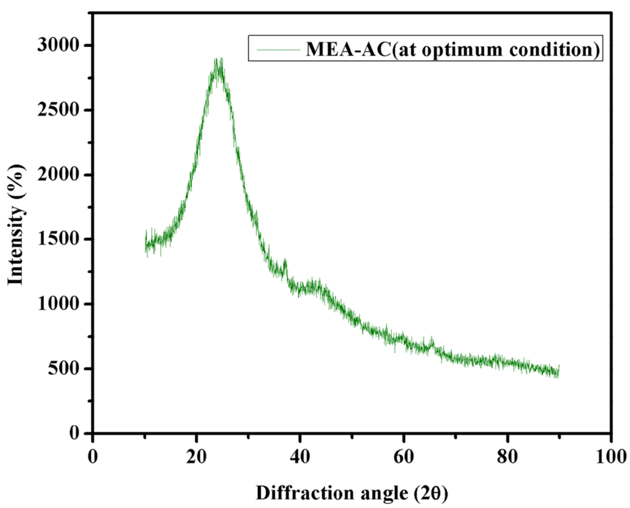

Fig. 14 XRD Analysis of MEA-AC (at optimum condition)

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