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CO_2 Adsorption and Desorption studies for zeolite 4A

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Abstract

Fossil fuel power plants generate carbon dioxide in huge amount, its capturing and storing has received widespread attention and is viewed as an indispensable action for CO_2 discharge reduction. In this study, CO_2 adsorption capacities were resolved for zeolite 4A. Breakthrough adsorption studies were done. Fix bed for carbon dioxide adsorption and desorption over zeolite 4A has been consider. Zeolite characterized by ultraviolet and unmistakable spectrometers, X-beam diffraction (XRD), surface area zone of the adsorbent measured by standard strategy for Brunauer, Emmett and Teller (BET) by Nitrogen adsorption strategies and thermogravimetric investigation (TGA). The adsorption behaviour of carbon dioxide (CO_2) on these adsorbents was explored at 30^0C, 55^0C, 70^0C. Adsorption limit has been found for zeolite 4A at 30^0C, 55^0C, 70^0C. is 336.77, 607.2, 406.38 mg/gm of zeolite individually for given technique for adsorption. CO_2 desorption has been studied.

Keywords: Adsorption, desorption, break through capacity, XRD, Carbon dioxide.

Introduction

Burning of fossil energizes lead the release of CO_2 to the climate, which is accepted to cause global warming. Fossil fuel based power plants emits carbon dioxide, its capturing has received widespread attention and is viewed as a crucial approach for CO_2 emission reduction. CO_2 is by far one of the greenhouse gases being responsible for about 64% rise in greenhouse effect[1]. The introduction pollutants which causes harm to humans or other living organisms like chemicals, particulate matter, or biological materials that is air pollution[2]. Pollution is considered one of the main problem around the world[3]. Natural contamination and its effect on plant have very much perceived. The role of air pollutants causing injury to plants[4-5]. To decrease released carbon dioxide to atmosphere from stationary sources like power plants, fuel is of critical importance[6]. In separation and purification process adsorption is one of the effective technique. Adsorption of gasses on smaller scale permeable adsorbents is receiving increased attention in view of the importance of removal and recovery of CO_2. In this era utilization of a lot of fossil fuels has become one of the need of human, which lead to most serious global environment problems, which is now required to be seriously addressed worldwide[7-10].

This work is focused on studying of adsorbent capacity for CO_2 capture In this study, the mesoporous cylindrical particles were chosen as adsorbents to study adsorption performance of CO_2, and breakthrough or dynamic ,method performed[11-12]. One of the effective option for CO_2 capture is solid adsorbents adsorption. Sorbents with high adsorption capacity are desired For viable applications on the other hand, the accomplishment of this methodology relies on upon the determination of an adsorbent adsorption capacity with a high CO_2 selectivity. Characterization, CO_2 adsorption capacity and desorption study of the 4A zeolite[13-15]. Zeolites are utilized broadly as a part of numerous mechanical applications mainly in adsorption, catalysis and gases separation and ion exchange purposes[16]. Adsorption and desorption of CO_2 over zeolite 4A has been studied [17].

Material and Methods

Zeolite are crystalline, hydrated alumino-silicates of I and II group components, specifically, sodium, potassium, magnesium, calcium, barium and strontium[9]. Fundamentally, zeolites are structure alumino-silicate silicate which are based on infinitely extending three dimensional AlO_4 and SiO_4 tetrahedral linked to each other by sharing all the oxygen. They can be represented by the observational equation M_2/nO . Al_2O_3 . x SiO_2. yH_2O in this equation, x is for the most part equivalent to or more prominent than 2 since tetrahedral are joined only to tetrahedral SiO_4 and, n is the valency of the cation[4]. Zeolite 4A in the form of pellets of more or less 1 mm. Adsorbent was bought from Merck, India ltd. Carbon dioxide (15%) was secured from Sirin Gasses, Nagpur, India. GC grade ultra unadulterated He (99.99%) was gotten from Chemito Technologies, Nashik, India for directing the adsorption studies[18].

Characterization of Material: Zeolite 4A was described, utilizing distinctive characterization procedures. X-ray diffraction has been studied utilizing a diffractometer which is of Phillips Analytical Xpert, with monochromatic Cu Kα

radiation (λ = 1.54 Å)[18]. The adsorbents were investigated in a 2θ scope of 5^0–60^0 [19-21].

A BET surface range analyzer (Model No. ASAP 2020) furnished, product was used to focus the N_2 BET surface area. At 90^0C adsorbents evacuated. Further adsorbent lead to -196^0C temperature for N_2 adsorption. The BET surface region and volume of pore was controlled by utilizing the single point adsorption[21].

UV-VIS-Spectra of the material were recorded using an Ultraviolet and visible spectrometers carry instrument 1.12 version. The sample was analyzed in the wavelength between 200-800 nm.

Thermogravimetric examination performed utilizing a Rigaku-TAS-200 equipment to consider the thermal strength and dehydration attributes of the incorporated adsorbents. Around 25 mg of the adsorbent was kept in Thermo Gravimetric container and was warmed at a rate of heating 5^0C/min in an ambient environment. The adsorbent was warmed from ambient temperature to 500^0C. It can be seen from the curve, the weight reduction and the weight reduction rate (dW/dT) was recorded[18].

CO_2 Adsorption Studies: Breakthrough adsorption curve technique used for CO_2 adsorption examined. The (BTC) breakthrough adsorption curve technique was selected as the assessment strategy due to its various advantages. What's more, this strategy offers a particular point of preference to focus and determine adsorbent capacity by dynamic adsorption study and evaluate in practical way, i.e., fixed bed, flow system. This method can be used to study a simulated flue gas stream as described in previous studies[21-22]. The experimental set up had adsorption column was design (height = 66 cm, diameter = 9 mm), mass flow controllers (Aalborg, USA), sample selector valve, gas chromatograph (Model GC 7610). In a experimental evaluation protocol, dry adsorbent was pre-treated in Helium gas flow (35 ml/min) for 2h at adsorption temperature itself and contacted with 15 vol% CO_2 gas in He balance at a total flow rate of 52 ml/ min. The outlet was persistently observed utilizing GC–TCD fitted with Porapak-Q section and the adsorption break through point was resolved for Zeolite 4A was contemplated for CO2 adsorption[18]

CO_2 Desorption studies: After saturation of zeolite 4A with CO_2, bed temperature raised to (100^0C) and Helium flow started (35 ml/min) and GC reading noted after an hour He flow stopped and bed temperature raised to 150^0C and again Helium flow started (35ml/min) for an hour and complete CO_2 desorption studied, experimental setup was same as adsorption studies.

Results and Discussion

Characterization: The adsorbent zeolite 4A characterization was studied. Adsorbent underwent for XRD which predicts, structural property of zeolite matrix shown in Figure-1. Obtained Similar as per reference[18].

Figure 2 shows the UV-Vis spectra for base line, zeolite 4A.From figure it can be observed the peak appears at frequency 750-800 nm was observed in spectra of zeolite 4A

The specific surface area of zeolite 4A measured by the standard method of Brunauer, Emmett and Teller (BET). This method based on the physisorption of a gas on the adsorbent surface[3]. The specific surface area of the catalyst has been estimated using BET surface area analyzer of make Micromerities:ASAP-2020. The sample were degassed at 70-110^0C. Table-1 Presents a tabular representation of the surface area of the zeolite 4A.

Table-1
Surface area of adsorbent by BET method

Adsorbent	BET Surface Area (m^2/g)
Zeolite 4A	422

Weight reduction and thermal steadiness of the material as for temperature has been contemplated by Thermo-gravimetric Analysis (TGA), utilizing Rigaku TAS-200 apparatus.TGA investigation were performed from ambient temperature to 500^0C at warming rate of 5^0C/min at ambient conditions.

It can be seen from TG profile as indicated in figure-3, that 4A zeolite shows weight reduction till 400^0C. It has been accounted for that, zeolite show lack of hydration till 350^0C[18]. However this temperature is depend on the warming rate utilized as a part of the investigation. As a higher warming rate was utilized as a part of the present study, complete drying out was seen at nearly higher temperature. Introductory desorption of adsorbed moisture and different volatiles was seen in the adsorbents. It can be seen in this cases that there is vicinity of single ceaseless weight reduction "step" from room temperature to 400^0C If there should be an occurrence of zeolite this has been balanced out by aggregate weight reduction of 19.23%. Weight reduction is seen to be 9.05%. TG profile given in figure-3 zeolites 4A show weight reduction till 400 ^{0}C. zeolites exhibit dehydration till 350^0C has been reported[18].

CO_2 adsorption capacity of the zeolite: The consequences of the CO_2 adsorption studies utilizing the breakthrough method are exhibited in table-5

1 g dry zeolite was pre-treated in Helium gas stream (35 ml/min) at 30^0C for 2h, adsorption temperature (30^0C) and reached with 15 vol% CO_2 gas in He adjust at an aggregate stream rate of 52 ml/min. The outlet was continuously monitored using GC–TCD fitted with Porapak-Q column and the adsorption breakthrough point was determined for Zeolite 4A was studied for CO_2 adsorption[18]. Results for present system are enlisted in table-2

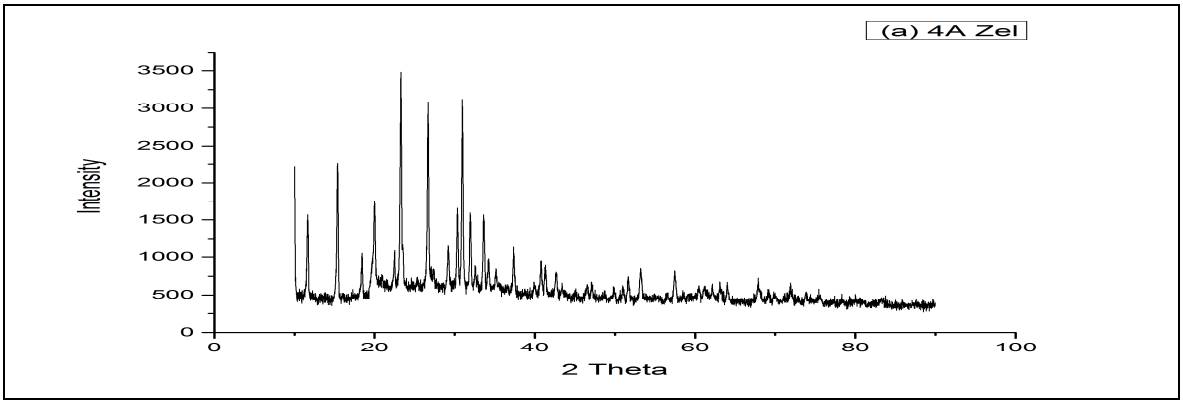

Figure-1
XRD of Zeolite 4A

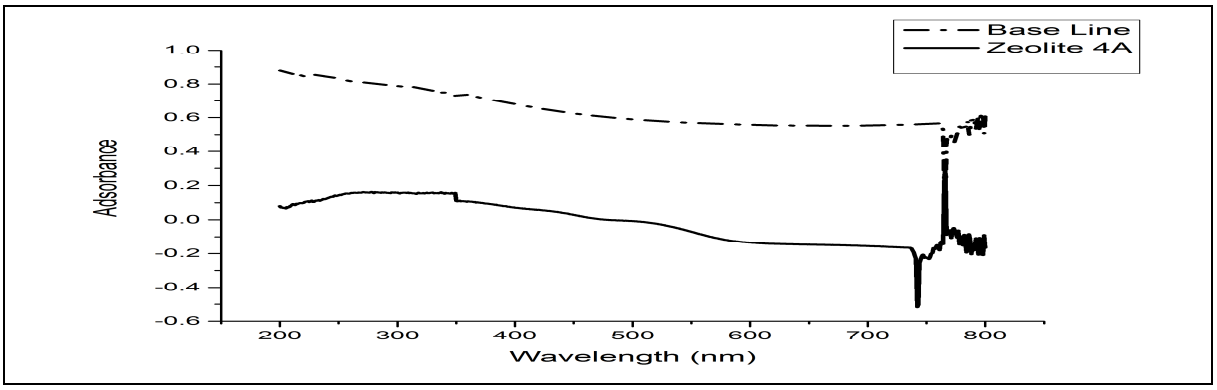

Figure-2
UV-VIS spectra for Zeolite 4A

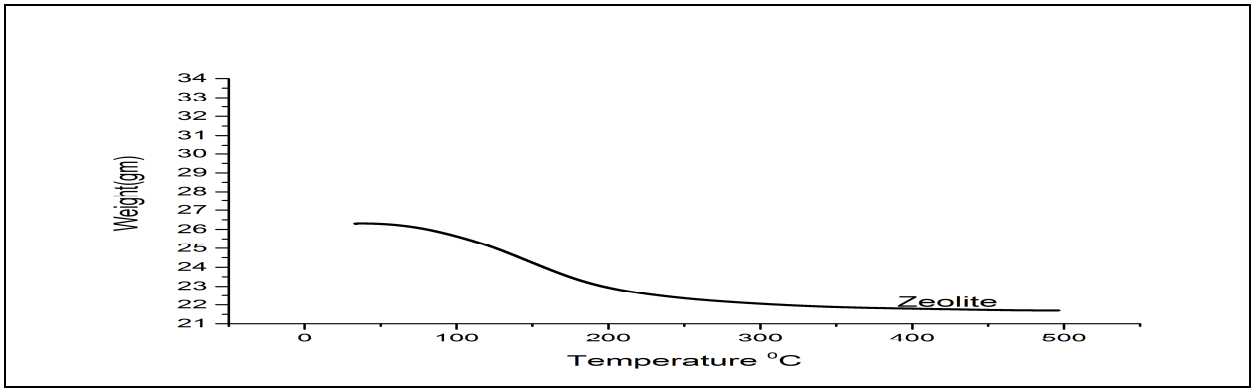

Figure-3
Representation of TG profile for 4A Zeolite

1 g dry zeolite was pre-treated in Helium gas stream (35 ml/min) at 55^0C for 2h, adsorption temperature (55^0C) and reached with 15 vol% CO_2 gas in He adjust at an aggregate stream rate of 52 ml/min. The outlet was continuously observed utilizing GC–TCD fitted with Porapak-Q section and the adsorption breakthrough point and saturation point was determined for Zeolite 4A as well studied for CO_2 adsorption[18]. Results for this system are enlisted in table-3.

1 g dry zeolite was pre-treated in Helium gas stream (35 ml/min) at 70^0C for 2h, adsorption temperature (70^0C) and reached with 15 vol% CO_2 gas in He balance at a total flow rate of 52 ml/ min. The outlet was ceaselessly observed utilizing GC–TCD fitted with Porapak-Q section and the adsorption breakthrough point and saturation point was estimated for Zeolite 4A studied for CO_2 adsorption[18]. Results for this system are enlisted in table-4.

Table-2
Breakthrough adsorption experimental readings at 30 ^{0}C

Sr No	Time(min)	30 ^{0}C		Sr No	Time (min)	30 ^{0}C	
		Ret Time	Peak Area			Ret Time	Peak Area
1	2.5	0	0	21	52.5	1.442	209872
2	5	0	0	22	55	1.442	209733
3	7.5	1.453	25119	23	57.5	1.441	210232
4	10	1.452	66517	24	60	1.441	210030
5	12.5	1.45	108159	25	62.5	1.441	210059
6	15	1.448	144453	26	65	1.441	210775
7	17.5	1.446	169377	27	67.5	1.441	210568
8	20	1.445	184916	28	70	1.441	210668
9	22.5	1.444	193844	29	72.5	1.441	211167
10	25	1.443	198933	30	75	1.441	211239
11	27.5	1.443	202292	31	77.5	1.441	211145
12	30	1.443	204857	32	80	1.441	211489
13	32.5	1.443	206507	33	82.5	1.441	211876
14	35	1.443	207247	34	85	1.441	212057
15	37.5	1.442	208011	35	87.5	1.441	212083
16	40	1.442	208349	36	90	1.441	212261
17	42.5	1.442	208822	37	92.5	1.441	212213
18	45	1.442	208831	38	95	1.441	212231
19	47.5	1.442	208791	39	97.5	1.441	212281
20	50	1.442	209169	40	100	1.441	212796

Table-3
Breakthrough adsorption experimental readings at 55 ^{0}C

Sr No	Time (min)	55 ^{0}C		Sr No	Time (min)	55 ^{0}C	
		Ret time	Peak Area			Ret time	Peak Area
1	2.5	0	0	21	52.5	1.452	215947.2
2	5	0	0	22	55	1.452	215854.1
3	7.5	0	0	23	57.5	1.452	215729
4	10	0	0	24	60	1.451	215573.4
5	12.5	0	0	25	62.5	1.45	215654.9
6	15	1.451	116925.8	26	65	1.45	215797.2
7	17.5	1.452	171403.2	27	67.5	1.45	215828.2
8	20	1.452	195747.4	28	70	1.45	216092.4
9	22.5	1.452	205718.1	29	72.5	1.45	216285.6
10	25	1.452	211964.2	30	75	1.451	216072.7
11	27.5	1.451	212118.5	31	77.5	1.451	215773.7
12	30	1.451	213321.3	32	80	1.451	216068.4
13	32.5	1.451	214467.8	33	82.5	1.451	216409.3
14	35	1.451	214320.5	34	85	1.451	216162.2
15	37.5	1.451	214769.4	35	87.5	1.451	216931.8
16	40	1.451	214578.5	36	90	1.451	216655
17	42.5	1.451	214929.1	37	92.5	1.451	217196.1
18	45	1.451	215010.4	38	95	1.451	216454.9
19	47.5	1.451	215120	39	97.5	1.451	216153.2
20	50	1.452	215251.2	40	100	1.451	216436.1

Table-4
Breakthrough adsorption experimental readings at 70 ^{0}C

Sr No	Time (min)	70 ^{0}C		Sr No	Time (min)	70 ^{0}C	
		Ret time	Peak Area			Ret time	Peak Area
1	2.5	0	0	21	52.5	1.449	213824.2
2	5	0	0	22	55	1.449	213412
3	7.5	0	0	23	57.5	1.449	213104.6
4	10	0	0	24	60	1.449	213030.1
5	12.5	1.455	170021.3	25	62.5	1.448	213490
6	15	1.449	210486.3	26	65	1.448	213705.5
7	17.5	1.448	212546.3	27	67.5	1.448	213539.8
8	20	1.447	212925.2	28	70	1.448	213773.2
9	22.5	1.448	212994.8	29	72.5	1.446	213960.9
10	25	1.449	212110.1	30	75	1.446	213813.8
11	27.5	1.448	212316.8	31	77.5	1.446	214036.2
12	30	1.449	212210.4	32	80	1.446	214307.3
13	32.5	1.449	212751.9	33	82.5	1.446	214270.9
14	35	1.449	212889.3	34	85	1.446	214324.1
15	37.5	1.449	213029.6	35	87.5	1.446	214279.1
16	40	1.449	213711.9	36	90	1.446	214277
17	42.5	1.449	213644	37	92.5	1.446	213999
18	45	1.449	213234.5	38	95	1.446	213987
19	47.5	1.45	213234.5	39	97.5	1.446	211456
20	50	1.449	213429.5	40	100	1.446	214256

Table-5
BTC, BT, ST, STC evaluated from the Break-through dynamic experiments at 30^{0}C, 55 ^{0}C, 70^{0}C for Zeolite 4A

Temp ^{0} C	Material	BT	BTC	ST	STC
30	Zeolite 4A	27.5	336.77	87.5	964.48
55	Zeolite 4A	22.5	607.2	100	2632.52
70	Zeolite 4A	15	406.38	97.5	2563.44

Notation, BT and ST –breakthrough time and saturation time respectively in min. BTC and STC-breakthrough capacity and saturation capacity in mg/gm of zeolite

Breakthrough Adsorption and Desorption Curve: Adsorption of CO_2 was studied using breakthrough adsorption curves method. CO_2 passed over adsorbent and GC reading was observed continuously and noted. Reading obtained are plotted gives breakthrough curve of zeolite is shown in figure-4. From break through curve it is observed that curve is parallel to x axis initially and at break through point, curve suddenly rises and continues till saturation of adsorbent. Nature of curve is different at different temperatures. In this way breakthrough point as well as saturation point were estimated. Desorption of adsorbed CO_2 was carried out as per current method and reading were noted from GC, plotted gives curve shown in figure-5. From desorption curve can be seen that, desorption increases as temperature increases.

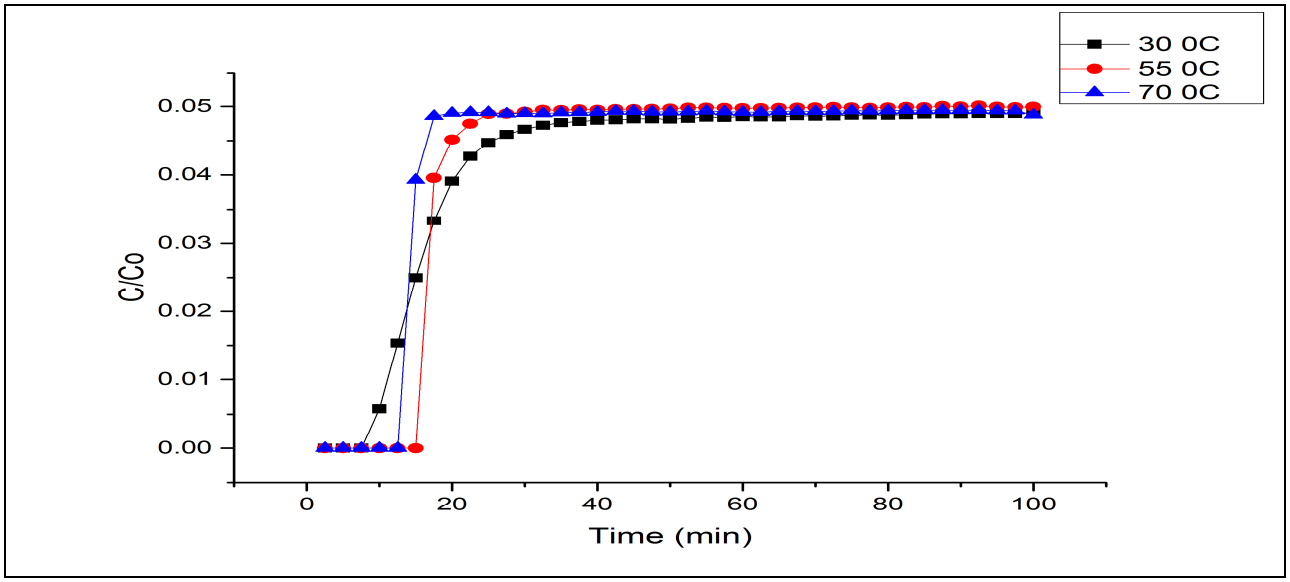

Figure-4
Breakthrough adsorption curves of CO_2 at different temperatures for zeolite 4A

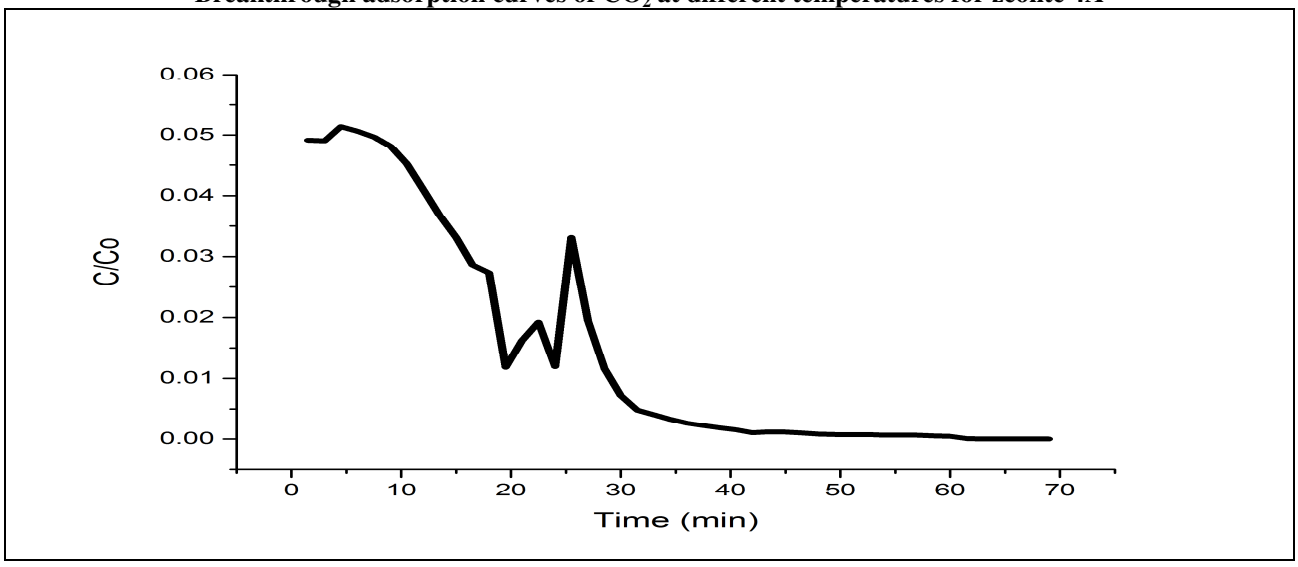

Figure-5
Desorption curves of Carbon dioxide on zeolite 4A

Conclusion

Zeolite had been analyzed for estimation of CO_2 adsorption capacities. The method of breakthrough curve was identified for present work reflects an attempt to mitigate the capture of CO_2. Adsorption capacity has been found for zeolite 4A at 30^0C, 55 ^{0}C, 70^0C is 33.6, 60.72, 40.6 mg/gm of zeolite respectively. From present study we can conclude that CO_2 adsorption capacity for zeolite 4A obtained better at 55^0C. Present study described the various characterization techniques applied for the selected functionalized adsorbent. The characterization details of 4A zeolite have also been studied in presented work. Different techniques were used for the characterization of this adsorbents. Carbon Dioxide desorption curve also obtained by carbon dioxide desorption from zeolite 4A.

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