Functionalised Adsorbents for Carbon dioxide Capture

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Abstract

Carbon dioxide is a green house gas and its emissions from large stationary sources like coal based power plants is a global catastrophe. Keeping in view the limitations associated with the reported adsorbents, development of new functionalised adsorbents based on immobilized amines is attempted in the present work. The synthesised adsorbents were thoroughly characterised using various techniques namely XRD, SEM, FTIR to determine the physico-chemical, structural and morphological properties before and after modification. The characterisation results have confirmed that the ordered porous structure of zeolite was retained after modification of only the surface and retaining the porosity and pore volume which is highly desired for an efficient adsorbent. These functionalised adsorbents were evaluated using continuous flow through packed bed reactors and simulated stream of ~15% CO_2 rest N_2 to determine adsorption capacity and other breakthrough parameters. It was observed that after incorporation of amines, the adsorption capacity of zeolite was significantly improved and was comparable to the benchmark adsorbents. The results clearly demonstrate high uptake of CO_2 in amine treated zeolite, almost in the temperature range of flue gas (50-120ºC). The investigations based on amine modified zeolites are promising showing better adsorption capacities and selectivities and are expected to overcome the limitations of conventional adsorbents.

Key words: *Carbon Dioxide Capture, Amines, Zeolites*

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1. Introduction

The phenomenon of global warming can be attributed to the greenhouse effect caused by the major greenhouse gases such as carbon dioxide, chlorofluorocarbons (CFCs), N_2O, methane, etc.

Carbon dioxide is a major contributor to this global phenomenon. CO_2 gas molecules by virtue of their polar nature tend to trap the infrared radiations arising from the earth's atmosphere resulting in warming of the earth and rise in surface temperatures. This is similar to the warming effect produced in a greenhouse. It has been predicted that global warming can cause a 3 °C rise in surface temperature by 2050 AD [1]. As per the Third Assessment report of the Intergovernmental Panel on Climate Change (IPCC), the present ambient concentration of CO_2 is about 380 ppm, as compared to 280 ppm in the pre-industrial revolution period (early 1900) [2].

To tackle this alarming global phenomenon, there is a growing need to develop suitable carbon capture and sequestration (CCS) technologies. The developed CCS technologies must be capable to capture CO_2 arising from the combustion of fossil fuels, as in power generation, or from the preparation of fossil fuels, as in natural-gas processing. The technologies developed may be also applied to other related issues such as, the combustion of biomass-based fuels and in different industrial processes, such as the production of hydrogen, ammonia, iron and steel, or cement. Capturing CO_2 involves the separation of CO_2 from some other gases present in the flue gas stream of a thermal power plant. It is equally important that the CO_2 captured needs to be transported to a storage site where it can be stored for a long period of time [3].

1.1 Capture CO_2 through Adsorption

Adsorption is a surface phenomenon as compared to absorption which is a bulk phenomenon. It is caused by the interaction of intermolecular forces between the gaseous phase and the surface of certain solid materials. The gaseous phase is referred to as adsorbate whereas the solid surface is referred to as adsorbent. Selective adsorption of gases is dependent on many factors such as the pore size of the adsorbent, dipole moment of the adsorbate, temperature and partial pressure of the gas involved. Adsorption may again be classified as physisorption and chemisorption depending upon the nature of interaction of the gas molecules with the solid surface. Physisorption is generally due to weak van der Waals' forces of attraction between the gas and the solid. In case of chemisorption, the interaction is chemical in nature and thus stronger. Solid materials having porous nature and high surface area tend to be good adsorbents. In this process, the adsorbent adsorbs a particular adsorbate to a certain extent, which is referred to as the adsorption capacity of the material. As the adsorbent gets saturated with the adsorbate, the material is regenerated so as to repeat the cycle of adsorption. Depending upon the method of regeneration used, adsorption processes may be further classified as pressure swing adsorption (PSA), temperature swing adsorption (TSA) and electric swing adsorption (ESA).

In PSA processes, the regeneration is affected by reduction in pressure. In TSA processes, regeneration is achieved by raising the temperature of the adsorbent whereas in case of ESA processes, regeneration is achieved by passing a low - voltage current through the adsorbent. PSA and TSA processes are widely used in H_2 production, separation of O_2 and CO_2 from natural gas [6]. A combination of both these processes described as PTSA has been studied at pilot scale levels by the Tokyo Electric Power Company (TEPCO) & Mitsubishi Heavy Industries for zeolite Ca-X (β) [7].

Different adsorbent materials have been investigated which include zeolites, activated carbons, pillared clays and metal oxides [8-20]. Siriwardane et al. have reported high adsorption capacities to the tune of 160, 135 and 110 mg/g for zeolites 13X, 4A and activated carbon respectively at 25°C and 1 atm CO_2 partial pressure. However, it was observed that with increasing temperature, as comparable to that of flue gas streams this capacity drops down drastically. Thus, these adsorbents need to be modified so as to facilitate chemical adsorption and therefore there is an increasing demand to design highly selective adsorbents, which can operate at high temperatures [21]. Also, there is a need to develop adsorbents that may be able to perform in the presence of steam with improved selectivity towards CO_2 [22].

2. Methodology

Considering the acidic nature of CO_2 it is envisaged that incorporation of basicity in the adsorbent, can improve the adsorption behaviour for enhanced uptake of CO_2. This concept can be understood by the use of the conventional amine systems for absorption of CO_2. Amines have been used in the past, in liquid absorption systems to remove acidic gases like CO_2, SO2, etc. which is actually a chemical reaction. Therefore incorporation of basic molecules like amines on the conventional adsorbents like zeolite, activated carbon and alumina can promote the adsorption capacity of the support matrix. This may be attributed to the additional process of a weak chemisorption process taking place along with the physisorption process which may be attributed to the support matrix.

2.1 Synthesis of adsorbents

Synthesis of amine modified sorbents has thus become a research issue to be investigated by different researchers in the area of carbon capture. Several possible matrix-functionalization molecule combinations have been tried and reported by our group at CSIR-NEERI. A brief description of synthesized adsorbents is discussed in the following section.

2.1.1 Amine functionalized zeolite-13X

The immobilization of amines was also carried out using alcoholic solutions of amine. The amine solutions with different concentrations corresponding to 25, 50 and 80 weight percent loadings were prepared in methanol. The zeolite was wetted with methanol prior to agitation with amine solution by agitating zeolite 13X beads and methanol in solid liquid ratio of 1:2 for a period of 10 minutes in two stages. The wetted beads were then air-dried and then agitated with alcoholic amine solution for a period of 15 minutes and 4 hours on a rotary shaker at ambient temperature, keeping the solid liquid ratio at 1:2. The amine solution was decanted and stored for analysis whereas the zeolite beads were allowed to dry in air overnight.

2.2 Evaluation technique

Among several options for post combustion CO_2 capture, flow through column adsorption processes are considered to have high potential for capturing CO_2 gas from bulk flue gas. The bed is filled with sorbent, which is a material used to adsorb gases. The sorbent characteristics include the possession of high internal surface area, controlled pore size, stable network structure and ability of modify surface chemical to suit specific applications.

All the as prepared adsorbents were evaluated for CO_2 adsorption at different temperatures namely 30, 55 and 75 °C. These temperatures were chosen keeping in mind that the best location for adsorption of CO_2 in a coal-fired thermal power plant is after the flue gas desulphurization (FGD) unit before the stack. Thus, these temperatures were selected as they represented the post-FGD region, which is typically around 55-75 °C. The selected screening temperature was 55 °C. The shortlisted matrices were then also evaluated at lower and higher adsorption temperature of 30 and 75 °C respectively.

2-2.1 Dynamic flow through system

In this method, the gas stream to be treated is passed over a fixed bed of adsorbent. An unsteady state condition prevails, in that the adsorbent bed continues to take up increasing amounts of adsorbate gases. The composition of the gas stream at the outlet of the bed is monitored continuously. Then the amount of a particular gas is followed as the fraction of the concentration of that gas in the effluent gas from the adsorption column Ce over that of the gas concentration in the feed gas, Co. This method matches practical (actual end use) conditions like flow conditions, temperatures and multi-component streams and we can calculate the dynamic adsorption capacities of the materials.

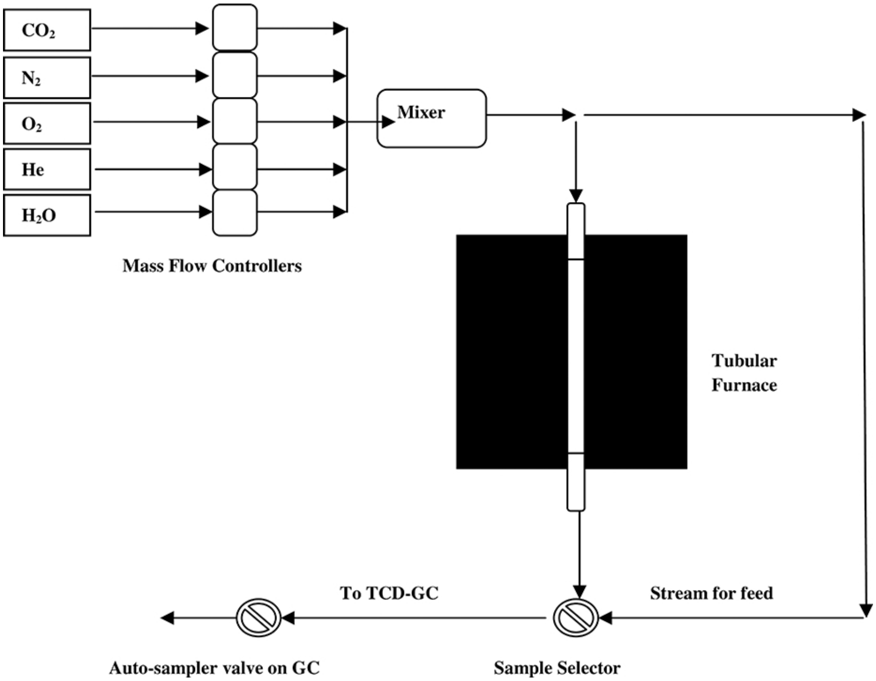

Figure 1. *Experimental setup used for breakthrough adsorption studies*

Table 1. *Adsorption bed (Column) configuration*

Parameters	**Values**
Bed length (mm)	340
Effective working length (mm)	300
Internal diameter (mm)	10
Wall thickness (mm)	2
Dead volume (ml)	25
Unused bed length (mm)	8
Unused bed volume (mm^3)	25

3. Characterization

The surface morphology of adsorbents needs to be investigated to suggest the role of adsorbent support and functionalization molecule towards CO_2 adsorption. Various adsorbent characterization techniques have been utilized to explain the possible happening over the surface of adsorbents due to functionalization and CO_2 adsorption.

3.1 X-ray diffraction (XRD) analysis

X-ray diffraction analysis was conducted to access the structural integrity of the adsorbent samples after incorporation of the amines. The low angle X-Ray diffraction patterns have been recorded using X-ray diffractometer, Model (Phillips: PW-1830). The radiations of Cu-Kα were generated using X-ray generator of model (PW 1729) of same make and the β radiation were filtered using monochromator. Rigaku: MiniflexII-DD34863 operated at 30 kV and 15 mA with a monochromator and using Cu-Kα radiation (k = 0.15418 nm) has also been used to obtain the XRD pattern of samples under the 2Θ range from 5 to 60°. The radiations of Cu-K_α were generated using X-ray generator of model of same make and the β radiation were filtered using monochromator.

3.2 Fourier transform infrared (FTIR) analysis

The IR spectra of the synthesized materials were recorded using a Perkin–Elmer spectrometer using the KBr pellet technique. The samples were analyzed in the wavelength region 4000–400 cm-1. This was done for confirming the formation of mainly the carbamate and bicarbonate groups which are formed as the adsorption product present in the adsorbent samples. The details of the functional groups before and after adsorption were an important tool to suggest the reaction mechanism taking place over the adsorbent with CO_2 interaction.

3.3 Flash Elemental analysis (EA)

The elemental analysis of the samples was determined by using a Thermo Flash EA 1112 fitted with a MAS 200R autosampler including instrument control. Data analysis was done with the help of Eager Xperience software package.

Elemental nitrogen (N), carbon (C), hydrogen (H), sulphur(S) content was analysed. Samples were measured in duplicate with laboratory standards and blanks. The instrument was first checked for helium pressure which was kept between 4 and 5 bars, and oxygen pressure at 4 bar. The gas pressure inside the instrument's gauges, inside the detector compartment was also set accordingly.

3.4 Scanning Electron Microscopy (SEM) analysis

Scanning electron microscopy (SEM) analysis was used to investigate the structural transformations of adsorbents. It was carried out to provide information on the association and distribution of elements within particles of adsorbents. Analysis was carried out using Quanta 600 Scanning Electron Microscope by FEI Company. The Quanta 600 SEM produces enlarged images of a wide variety of specimens, using magnifications usually from 100x to about 100,000x.

3.5 Thermogravimetric analysis (TGA)

Isothermal analysis of adsorbents was performed using thermogravimetric analysis (TGA) on a Perkin Elmer TGA. The thermo gravimetric experiments were carried out in a Quadstar (Perkin Elmer Instruments). It was capable of heating at the rate of approximately 200 °C min-1. The sample temperature was measured with a thermocouple placed very close to the sample.

3.6 BET surface area and pore size analysis

The standard method of Brunauer, Emmett and Teller (BET) was used for measuring specific surface area of the adsorbent based on the physical adsorption of a gas on the solid surface. Specific surface area of the catalysts has been determined using BET Surface Area Analyzer of make Micromeritics: ASAP-2000. The samples were degassed at 70-110°C. This temperature range was chosen keeping in mind the boiling point of the various amines used in the present study.

4. Results and discussion

4.1 Amine functionalized zeolite-13X

Synergistic effect of loading of various amines over the 13X zeolite is shown in fig 2. The first Y-axis shows CO_2 adsorption capacity per unit weight of adsorbent. Whereas, additional adsorption of CO_2 because of amine loading is depicted on second Y-axis and by area graph. In all samples the targeted loading of amines was 50% by wt of zeolite. However the actual loadings obtained were between 11 to 19% as detailed in Table 2. It is apparent from the data that the loading of bulkier amines namely DEA and EDAN resulted in reduction of adsorption capacity of 13X. A promotional effect was observed in case of MEA, EDA, IPA and AMP. The effective promotion by IPA and AMP was about 60 and 62 mg of CO_2 per g of amine loaded respectively. In case of MEA and EDA the promotional adsorption was 22 and 25 mg of CO_2 per g of amine loaded respectively.

Table 2. *Breakthrough adsorption capacities at 75 °C of 13X modified by different amines*

Sr. No.	**Material**	**Adsorption Capacity (mg/g)**	**Amine loading (wt.%) (titrimetric)**
1	13X-Comm.	16.01	-
2	13X-MEA-50	19.98	17.76
3	13X-DEA-50	2.91	12.19
4	13X-EDA-50	20.15	15.79
5	13X-IPA-50	22.78	11.10
6	13X-AMP-50	25.86	15.64
7	13X-EDAN-50	5.26	19.19

Adsorption temperature = 7 °C; gas flow rate = 52 c.c/min; CO_2 concentration = 11%

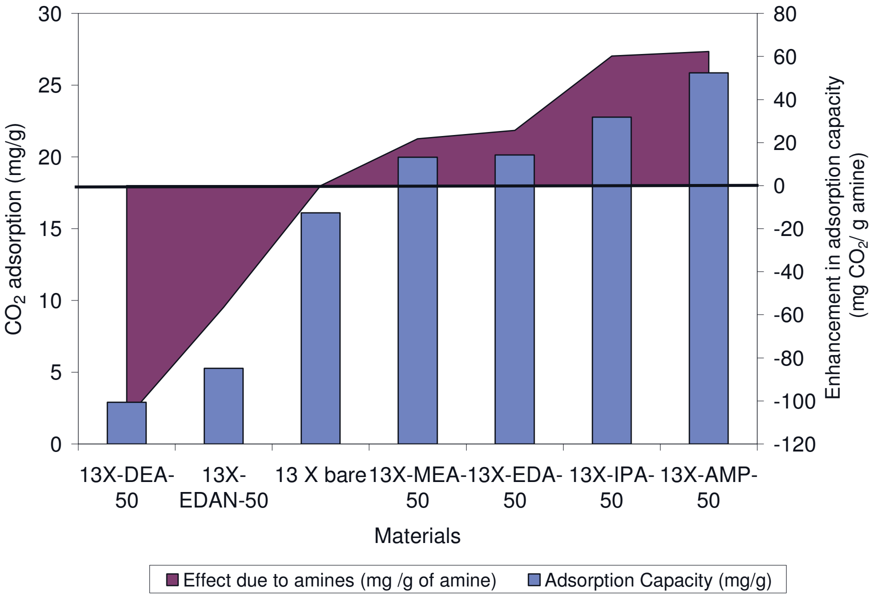

Figure 2. *Comparative adsorption capacities and amine efficiencies of different amines*

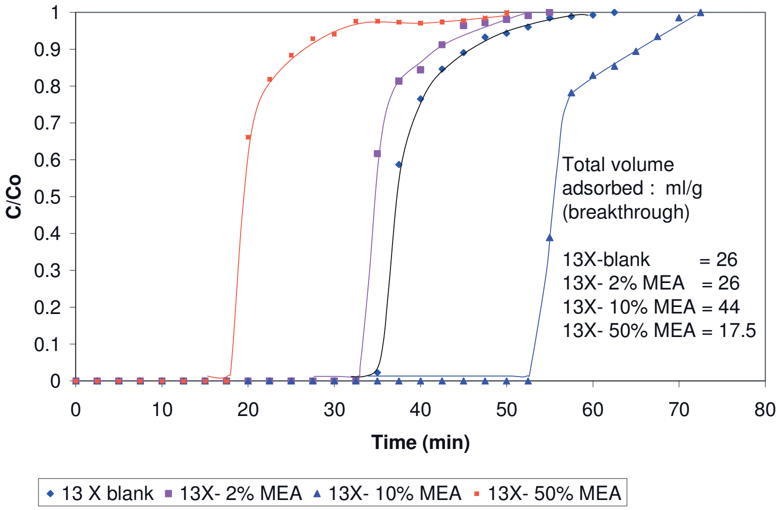

Figure 3. *Adsorption capacities of modified 13X at 30 ºC*

For adsorption at room temperature, 13X-10% MEA exhibited highest adsorption capacity 86.43 mg compared to 51.07 mg of blank. This proved enhancement in adsorption of acidic gas CO_2 with introduction of basicity with amine loading as reported by many researchers (Birbara, 1999 and 2000, Chang, 2003, Xu, 2005). As can be seen from Table 3, small loading (2%) had capacity unchanged. But even with very high loading (50%), capacity had dropped to 34.38 mg. This can be attributed to possible pore blocking and restricted access to adsorption sites for CO_2 at higher loadings.

Table 3. *Adsorption capacities of amine modified 13X at 30 ºC*

Material	**BT capacity**			**Saturation capacity**	
	c.c/g	**mmol/g**	**mg/g**	**mmol/g**	**mg/g**
13X-blank	26	1.16	51.07	1.44	63.33
13X-2% MEA	26	1.16	51.07	1.33	58.52
13X-10% MEA	44	1.96	86.43	2.08	91.73
13X-50% MEA	17.5	0.78	34.38	1.09	47.96

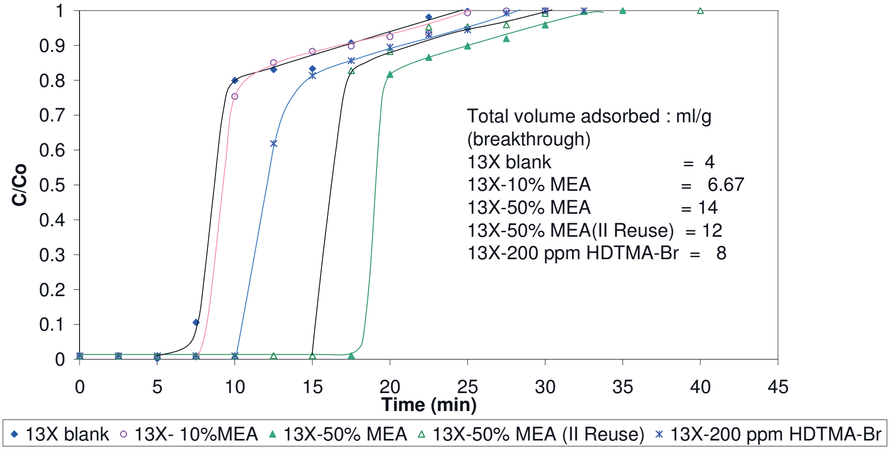

Figure 4. *Adsorption capacities of modified 13X at 120 ºC*

At 120 °C, higher loading (50%) proved to give highest adsorption capacity of 27.5 mg compared to 7.86 mg of blank and 13.1 mg for 13X-10% MEA. The surfactant modified 13X exhibited intermediate adsorption capacity of 15.71 mg.

Table 5. *Adsorption capacities of amine and surfactant modified 13X at 120 ºC*

Material	**BT capacity**			**Saturation capacity**	
	c.c/g	**mmol/g**	**mg/g**	**mmol/g**	**mg/g**
13X-blank	4	0.18	7.86	0.41	18.15
13X-10% MEA	6.67	0.30	13.10	0.47	20.76
13X-50% MEA	14	0.63	27.50	0.76	33.59
13X-50% MEA (II Reuse)	12	0.54	23.57	0.66	28.97

4.2 Representative characterization results

The select adsorbents from each category have been characterized to know about the surface morphological changes attributing towards improved CO_2 adsorption properties.

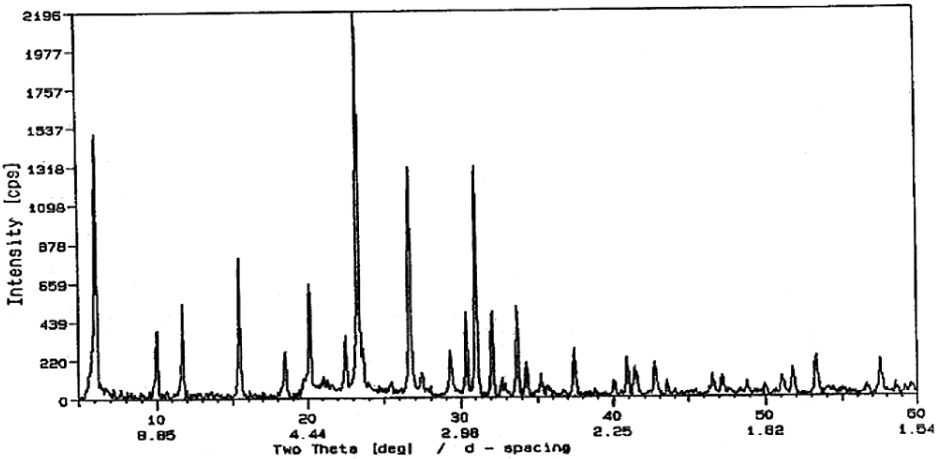

Figure 6. *X-ray diffraction pattern of 13X-AMP-25*

A representative characterization result pertaining to above explored adsorbents is provided as follows. The presence of carbamate species gets confirmed with the FTIR analysis at peak position 992.41 cm-1. This also supports the possible mechanism of amine CO_2 interaction towards carbamate formation reported in literature.

Table 10. *Surface area and pore volume of adsorbents*

S.N.	Adsorbents	BET surface area (m^2/g)	Pore volume (ml/g)
1.	13X zeolite matrix	359	0.22
2.	13X-AMP 25%	265	0.18

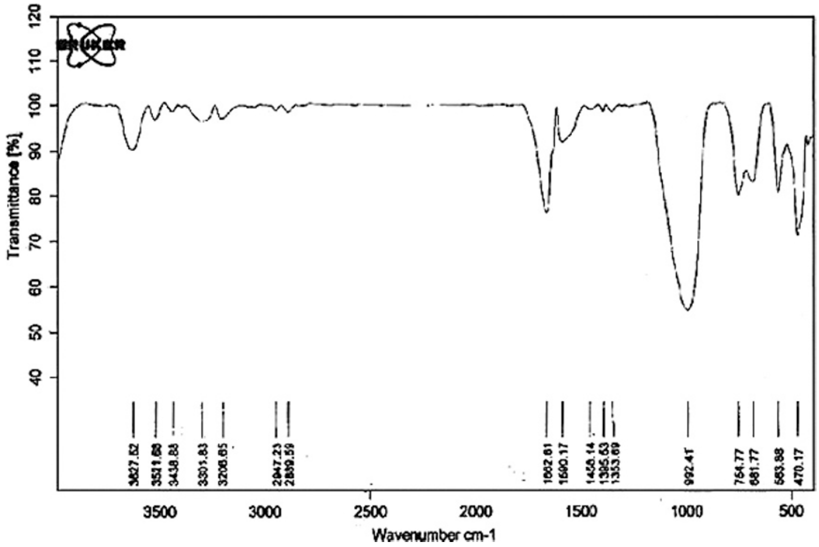

Figure 7. *FTIR spectrum of 13X-AMP-25 evaluated for adsorption of CO2*

5. Conclusions

The newly synthesized amine functionalised adsorbents based on zeolites have been evaluated and characterized for their adsorption performance in presence of binary CO_2/N_2 gas mixture. It was observed that the incorporation of amine significantly improves the adsorption properties of zeolite. Further, adsorption studies at different temperature indicate that the adsorption capacity of aminated zeolites decreases with increase in temperature. The functionalised zeolites also showed improved selectivity towards CO_2 in presence of water at temperatures of 55°C. Moreover, increase in adsorption capacity was observed in presence of moisture as compared to dry feed mixture and the functionlaised adsorbents showed adsorption capacities in range of 52 mg/g to 63 mg/g. The study has proved that functionisation of zeolites with amines overcomes the drawbacks namely low adsorption capacity, interference due to moisture and other gases, deleterious effect of temperature etc. associated with conventional adsorbents for CO_2.

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