Thesis

On

Modification of Conventional Adsorbents for CO_2 Capture

Submitted in partial fulfilment of the requirements for degree of

Master of Technology

In

Chemical Engineering

By:

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DECLARATION

I hereby declare that the thesis entitled **"Modification of conventional adsorbents for CO_2 capture"** is an authentic record of my study carried out as requirements for the award of degree of **M. Tech (Chemical Engineering)** at Thapar University, Patiala, under the guidance of Dr. P.K.Bajpai, Distinguished Professor, **Department of Chemical Engineering** and Dr. Haripada Bhunia, Associate Professor, **Department of Chemical Engineering**, Thapar University, Patiala during **June 2010 to June 2011.** The matter embodied in this thesis has not been submitted in part or full to any other university or institute for the award of any degree.

(TINESH CHAND)

This is to certify that the above declaration made by the student concerned is correct to the best of our knowledge and belief.

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Last but not least, I would like to thank God for all good deeds.

Tinesh Chand

ABSTRACT

Conventional adsorbents show high adsorption capacities at room temperature, their capacities decline with rise in temperature. Selectivity of these materials is low. Adsorption of these materials is physical adsorption rather than chemical adsorption. To overcome these limitations, conventional adsorbents need to be modified. CO_2 is a Lewis acid, introduction of Lewis bases onto surface of these adsorbents may favour CO_2 capture performance of these materials.

Modification of conventional adsorbents can be done by many methods like amination, activation, impregnation of Fe_2O_3 and Cr_2O promoted by Zinc on solid support. In this work, conventional adsorbents chosen was Zeolite 13X, while modification was done by monoethanol amine (MEA). Aqueous solutions of MEA of four different concentrations were prepared and agitated with crushed Zeolite 13X. Four different concentrations were 5 wt%, 10 wt%, 15 wt% and 20 wt% of MEA. Amount of MEA loaded on Zeolite13X were calculated by titrimetric analysis. Out of these solutions, 20 wt% MEA solution showed best loading. Breakthrough curves of bare Zeolite13X and modified Zeolite 13X were obtained with the help of adsorption column set up.

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CHAPTER 1

INTRODUCTION

Environmental issues are getting attention of the world today. Issue of greenhouse gases is getting increasingly important. Greenhouse gas is a gas in the atmosphere that absorbs and emit the radiation within thermal infrared range. The primary greenhouse gases in earth's atmosphere are water vapour, carbon dioxide, methane, nitrous oxide and ozone. Carbon dioxide is principle greenhouse gas thought to be responsible for global warming and climate change. Contribution of carbon dioxide in green house effect is 9-26%. Since about 1750, human activity has increased the concentration of carbon dioxide and other greenhouse gases. Measured atmospheric concentrations of carbon dioxide are currently 100 ppm higher than pre-industrial levels. Natural sources of carbon dioxide are more than 20 times greater than sources due to human activity, but over periods longer than a few years, natural sources are closely balanced by natural sinks mainly photosynthesis of carbon compounds by plants and marine plankton. As a result of this balance, the atmospheric concentration of carbon dioxide remain between 260 and 280 ppm for the 10,000 till the start of industrial area as shown in figure 1. The concentration of anthropogenic CO_2 in the atmosphere has been increasing since the start of industrialization in the 19th century, more rapidly during the second half of 20th century. Atmospheric CO_2 concentration is increasing, main contribution is by fossil fuel combustion for power generation, transport, industry and domestic use. Carbon stored in these fossil fuels is emitted mainly as CO_2, when these fossil fuels are burned to produce energy. The main fossil fuels burned by humans are petroleum oil, natural gas, and coal. Some industrial processes also lead to CO_2 emissions, specialized industrial processes such as mineral production, metal production, and use of petroleum based products can lead to CO_2 emissions (Roy et al., 2009)

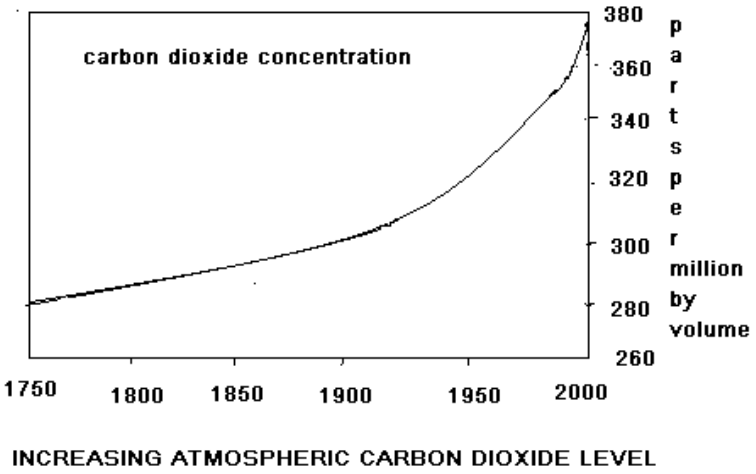

carbon dioxide concentration
380
360
340
320
300
280
260
parts per million by volume
1750
1800
1850
1900
1950
2000
INCREASING ATMOSPHERIC CARBON DIOXIDE LEVEL

Fig. 1

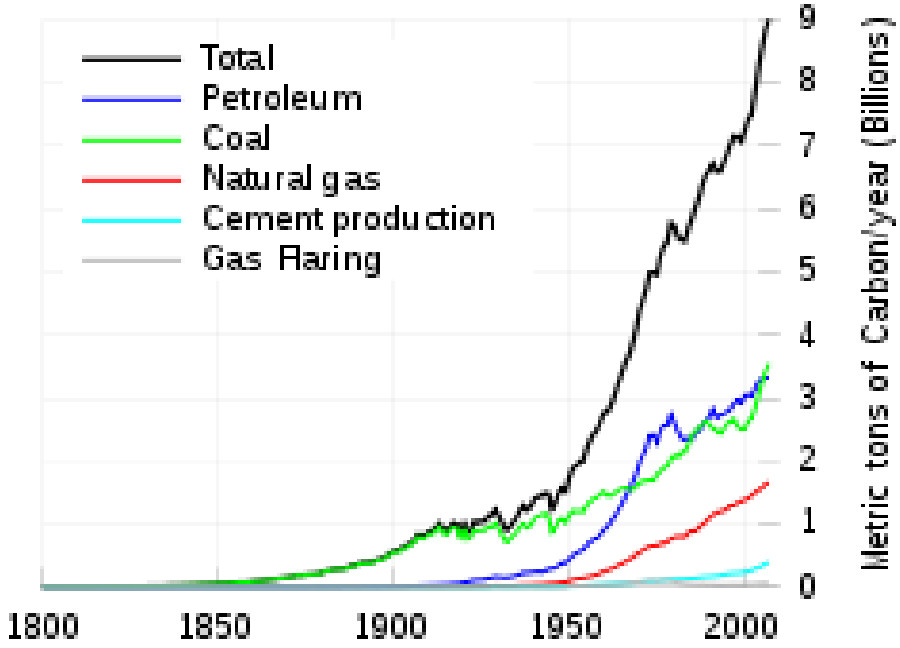

Total
Petroleum
Coal
Natural gas
Cement production
Gas Flaring
Metric tons of Carbon/year (Billions)
0
1
2
3
4
5
6
7
8
9
1800
1850
1900
1950
2000

Fig. 2

This has been assumed because there is increase in level of concentration of CO_2 in the atmosphere from preindustrial level of 280 to 377 ppm as reported by Yang, et al.(2008). This corresponds to a radiative forcing (the change in net irradiance, i.e. the difference between the incoming radiation energy and outgoing radiation energy in a given climate system at the tropopause) of 1.46 W/m^2. Amount of radiation which escapes, depends on the concentration of greenhouse gases in the atmosphere and when carbon emission is increased, it results in less escape of radiation. With the increase in level of CO_2 concentration, temperature of earth has increased by $0.6^oC+\_\ 0.2^oC$ over the last century. This may be the small increment, but the warming will increase with time and could have disastrous consequences. These might include the rise of sea level, a major effect on agricultural productivity, a reduction of ozone layer, increased extreme weather, spread of diseases, change in ecosystem, etc.(Roy et al. 2009).

Increasing awareness about reduction in greenhouse gases has led to many initiatives. One of such initiative is Kyoto Protocol. Kyoto Protocol is a protocol to the United Nation Framework Convention on Climate change (UNFCCC) aimed at fighting global warming. The protocol was initially adopted on 11 December 1997 in Kyoto, Japan and entered into force on 16 February 2005. As of July 2010, 191 states have signed and ratified the protocol. Under the protocol, 37 countries ("Annex l countries") commit themselves to reduction of four greenhouse gases, out of which one is CO_2. Annex l countries agreed to reduce their collective greenhouse gas emissions by 5.2% from the 1991 level. While the former US federal government opted against Kyoto type policies, the Obama administration has attempted some Kyoto protocol goals on a local basis. The white house announced on November 25, 2009 that Barrack Obama is offering a US target for reducing green house gas emissions in range of 17% below 2005 levels by 2020. Reduction in CO_2 emissions can be done by two methods, either by eliminating source of emissions using alternative method or by capturing CO_2 after emissions. It is not possible to replace fossils fuels by other fuel in near future, so post combustion capture of CO_2 is being researched. There are four main methods to capture CO_2 - Chemical absorption method, Membrane separation, Cryogenic separation, Adsorption process.

Chemical absorption has disadvantage of high energy penalty, solvent degradation, corrosion and need for pre-treatment to remove SO_X and NO_X. Membrane separation and cryogenic separation needs high energy in compression step.

CHAPTER 2

LITERATURE REVIEW

Conventional adsorbent available are like Zeolite 13X, Zeolite 3A, Zeolite 4A, Zeolite 5A, Activated carbon, Carbon molecular sieves. Modification of these adsorbents for their better adsorption of CO_2 and further regenerability is done by many methods. Out of these methods some published methods, their characteristics and their performance of CO_2 adsorption are being discussed in upcoming paragraphs.

2.1Amination

Amination is basically addition of amine groups on required substance to be modified. Different methods of amination can be said to as with ammonia gas, with the mixture of ammonia gas and air, by treatment with aqueous solution of amine, by treatment with organic solvent solution of amine.

For treatment with ammonia gas, raw almond shells were taken, grounded, sieved and particle size9 between 1mm and 3mm were selected. Raw almond shells were then carbonized in horizontal quartz reactor. Resulting char in batches was heated in N_2 flow in quartz micro reactor inside a vertical furnace equipped with temperature control. Char was exposed to a flow rate of 50 cm^3min^{-1} of ammonia at 800 ^{0}C. Exposure to ammonia gas for interval of 2 hour and 3hour were done and resulting char were designated as AN2 and AN3 for exposure of 2 hour and 3 hour respectively. Chemical analysis of these treated samples and untreated samples were carried out. Chemical analysis of these treated samples were untreated samples were carried out. Untreated samples showed N content of 0.4%. AN2 showed N content of 4.5% and AN3 showed N content of 5.1%. Textural parameters were calculated from N_2 and CO_2 adsorption isotherms at -196 ^{0}C and 0 ^{0}C respectively. AN_2, AN_3 has much higher value of total pore volume (Vp), BET surface area. Longer treatment time gives higher value of total pore volume and BET su7tyrface area. CO_2 adsorption capacities were evaluated in TGA in 50 cm^3/min of CO_2 flow at 25 ^{0}C and 100 ^{0}C. AN_2 and AN_3 show adsorption of 9 to 10%(wt%) at 25 ^{0}C and 3 to 3.5%(wt%) at 100 ^{0}C. With the increase in temperature, adsorption capacity decreases, (Plaza, et al, 2009). For treatment with mixture of ammonia and air, same char obtained from raw almond shells was used. It was brought into contact with flow rate of 50 cm^3/min of gas mixture of ammonia and air in a ratio of 1:2. Temperature was fixed at 300 ^{0}C to avoid combustion of char. Chemical analysis of modified compound was done. It showed N content of 4.0% and O

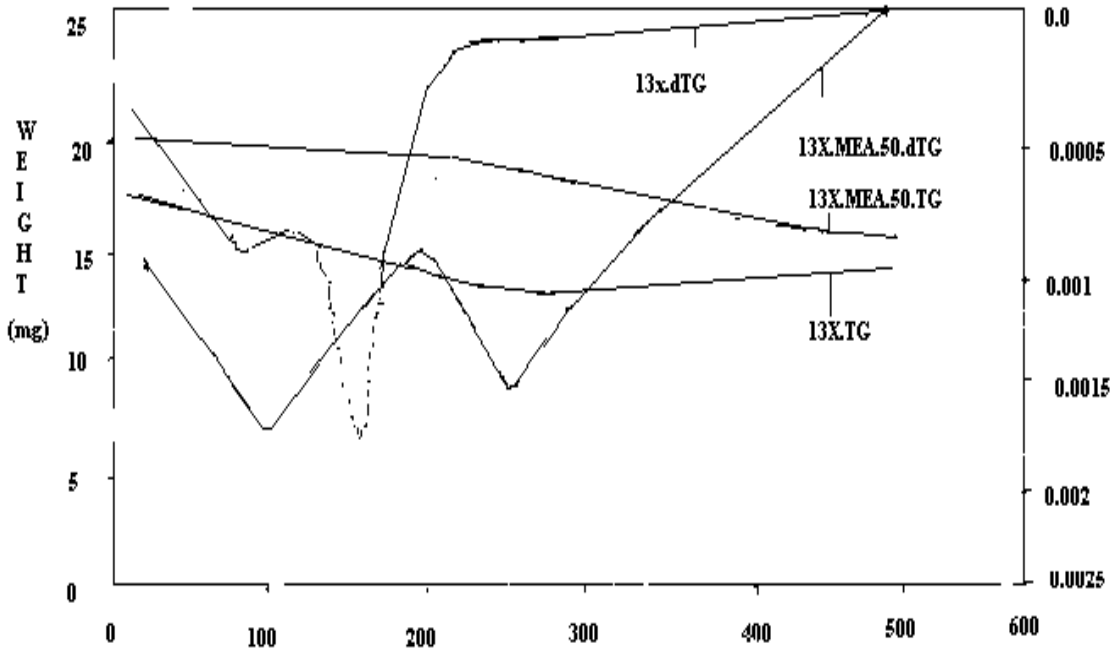
content of 7.8%. Temperature desorption test showed evolution of Nitrogen species(NH_3 and HCN). But in case of AN2 and AN3, there was no evolution of such compounds, this is because nitrogen was incorporated into thermally stable pyridines and pyrrole type functionalities in AN2 and AN3. (Pevida et.al., 2008). Textural parameters were calculated from N_2, CO_2 adsorption isotherms at -196 ^{0}C and 0 ^{0}C respectively. Modified compound has much lower value of total pore volume and BET surface area. (Plaza et.al., 2009). For treatment with aqueous solution of amine, three different solutions of monoethanol amine, ethylene diammine and isopropyl amine were prepared. These solutions are added to adsorbent in solid to liquid ratio of 1:2. Three different amine concentrations were taken 25, 50 and 80 wt%. The mixture was agitated on rotary shaker for three different periods of time (15 min, 2h and 4h). Amine solution was separated from adsorbent by centrifugation and air dried overnight. (Chatti et. al., 2009). Characterisation was done using different techniques. To assess the structural integrity of adsorbents after incorporation of different amines, modified adsorbents were analysed by Phillips Analytical Xpert diffractometer with monochromatic CuKa radiation. Powder X-ray diffraction studies were carried on modified adsorbent. BET surface area and pore volume was determined by using the single point adsorption method. A micromeretics BET surface area analyser equipped with Tristar software was used to determine the N_2 BET surface area and pore volume of modified adsorbents. Thermogravimetric was performed using a Rigaku-TAS-200 apparatus to study thermal stability and dehydration characteristics of the modified adsorbents. The IR spectra of modified adsorbent were recorded using a Perkin-Elmer spectrometer using the KBr pellet technique in the wavelength range of 4000-400 cm^{-1} (Chatti et.al., 2009).

Results of characterization

Characterization of Zeolite 13X and Zeolite 13X contacted with MEA solution of concentration 50 wt% was studied. The structural properties of amine loaded zeolite matrix and zeolite matrix was investigated by obtaining XRD patterns before and after amine incorporation. From the x-ray diffractogram of monoethanolamine (MEA), it was observed that structural integrity of zeolite 13X is maintained even after incorporation of amine (Chatti et al., 2009).

BET surface area and pore volume of zeolite 13X are 386.4 m^2/g and 0.2335 cm^3/g respectively. BET surface area and pore volume of MEA modified zeolite 13X are 14.9 m^2/g and 0.0441 cm^3/g. Reduction in pore volume and BET surface area of MEA modified zeolite 13X indicates that amine molecules have occupied the pore volume. (Chatti et al.,2009).

It can be observed from TG profile given in figure 3 , that unmodified 13X and MEA modified 13X zeolites show weight loss till 400 ^{0}C. It has been reported that, zeolites exhibit dehydration till 350 ^{0}C (Siriwardane et al., 2005). However this temperature is dependent on the heating rate used in experiment. As a higher heating rate was used in the present study, complete dehydration was observed at comparatively higher temperature. It was observed that in case of 13X, there is presence of only single continuous weight loss step from room temperature to 450 ^{0}C. This has



TEMPERATURE (0^{0}C)

Representative TG Profile of the adsorbents

FIG. 3

stabilized with a total weight loss of about 18.73%. A major weight loss is observed at 130 ^{0}C, which may be attributed to desorption of moisture in 13Xzeolite beads.In the case of MEA modified 13X, it has been observed that there are a total of three distinct weight loss steps at 70,150 and 240 ^{0}C. Since MEA has a boiling point of 170.8 ^{0}C, we may attribute the second weight loss between 120 and 200 ^{0}C to volatilization and degradation of MEA. The weight loss

is observed to be 5.63% in this region. A total weight loss of 22.56% is observed which is about 4% higher than the unmodified adsorbent (Chatti et al., 2009).

Determination of amine loadings

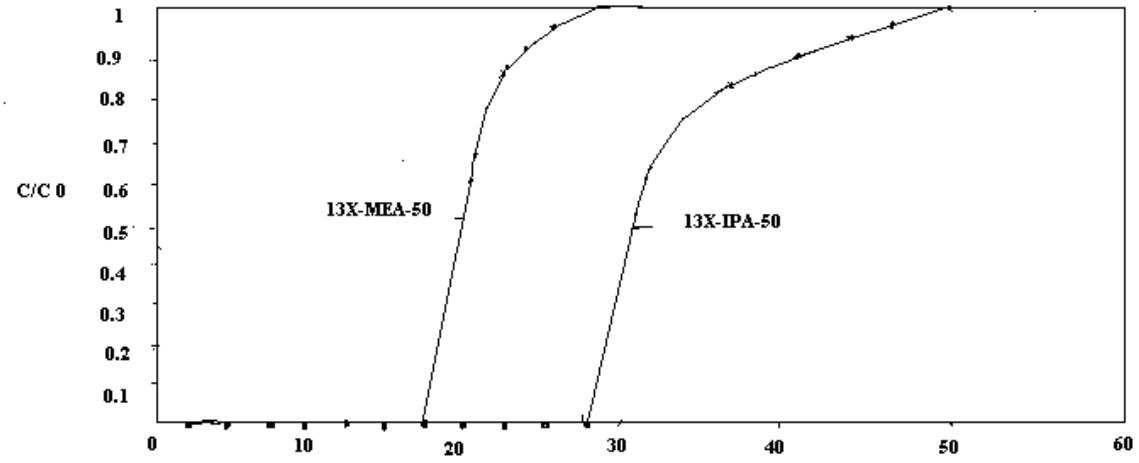
Amine loadings on the 13X zeolite beads were calculated by difference in amine concentration of solutions before and after treating with zeolite. The concentration of amines were determined using titrimetric analysis, gas chromatograohy (GC) and total organic carbon estimation (TOC).

Titrimetric method was used as described by Seaman and Allen method. According to this procedure, mixture of amine solution and glacial acetic acid was titrated against 0.1 N solution of perchloric acid in glacial acetic acid (Chatti et al., 2009).

Gas chromatographic determinations of amine were carried out with GC with Flame Ionization IUUwas used in the analysis. GC grade nitrogen was used as the carrier gas for the analysis. A calibration plot for each amine was plotted by injecting the known volume (1µl) of different molar solutions of amine. After plotting the calibration plot between the peak area and the molarity of the different amine solutions, the experimental solutions of each amine solution were injected and the estimation of the residual amine content was done (Chatti et al., 2009).

Since amine is a source of organic carbon, TOC technique can be used indirectly to estimate the amine content. The TOC of the initial and residual amine solutions were analyzed using a Non-Dispersive Infrared (NDIR) TOC analyzer (Chatti et al., 2009).

CO_2 adsorption studies



BREAK THROUGH CURVES OF CO2 ON MEA MODIFIED ZEOLITE 13X AND IPA MODIFIED ZEOLITE 13X – 75C

FIG. 4

CO_2 adsorption was studied using breakthrough adsorption curve method. The experimental set up had mass flow controllers, adsorption column (diameter = 1cm; height = 30cm), sample selector valve, 1 ml sample loop and gas chromatograph. In a typical evacuation protocol, 10 g dry adsorbent was pretreated in flow of He gas (20 ml/min) at 140 ^{0}C for 6 h, cooled to adsorption temperature (75 ^{0}C) and contacted with 15 vol% CO_2 gas in He balance at a total flow rate of 52 ml/min. The outlet was continuously monitored using GC-TCD fitted with Porapak-Q column and adsorption breakthrough point was determined. Zeolite 13X and Zeolite 13X modified with MEA and IPA at 50 wt% initial amine concentration were studied for CO_2 adsorption. Breakthrough adsorption capacity of zeolite13X, MEA modified (50 wt%) zeolite13X and IPA modified (50 wt%) zeolite13X are 16.01mg/g (mg of CO_2 adsorbed per gram of adsorbent), 19.98 mg/g and 22.78 mg/g respectively. It is observed that adsorption capacity of the amine loaded zeolite is increased by approximately 20-30 % in comparison with that of the bare zeolite matrix at 75 ^{0}C. As BET surface area and pore volume of amine loaded zeolite is lower as compared to unmodified zeolite, adsorption capacity of modified zeolite must decrease. But adsorption capacities of modified adsorbents are higher. This may be explained as

adsorption in case of modified adsorbents is chemisorption rather than physisorption. At ambient temperature, physisorption is dominant over chemisorption. Therefore at ambient temperature, surface area is vital key to the adsorption. At elevated temperature (75 ^{0}C in this study), chemisorption is dominant process due to incorporation of amine group in the zeolite. To support the values of adsorption capacities obtained by breakthrough method, CO_2 adsorption capacities were carried out using the volumetric adsorption principle. The experiments have been carried out at 1 bar guage pressure at 75 ^{0}C in presence of pure CO_2 stream. Equilibrium adsorption capacities using volumetric adsorption principle of 13X zeolite and MEA modified zeolite 13X are 37.33 mg/g and 48.64 mg/g respectively (Chatti et al., 2009)

For treatment with organic solvent solution of amine. The amine solutions with different concentration corresponding to 25, 50 and 80 wt% loading were prepared in methanol. The zeolite was wetted with methanol prior to mixing with amine solution by agitating zeolite 13X beads and methanol in solid to liquid ratio of 1:2 for a period of 10 min in two stages. The wetted beads were then air dried and then agitated with alcoholic amine solution for a period of 15 min and 4 h, 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 (Chatti et al., 2009).

Characterization was done by same method and by same instruments as done for aqueous solution of amine. Determination of amine loadings on zeolite were also done by same methods.

Effect of solvent on immobilization of amine

To understand the significance of solvent used in the modification, modification was done by using water and methanol as solvents for immobilization. Technique used for analysis is titrimetric method as it can be easily done in laboratory by simple set up. Water was used as solvent, as amines are soluble in water, it is a universal solvent and non hazardous. Methanol was chosen because of lower boiling point (64.7 ^{0}C) as compared to water (100 ^{0} C), which may facilitate proper drying of sample after immobilization. Using methanol would ultimately lead to uniform loading of amine on the zeolite matrix. Figure 8 compares the estimated MEA loading using methanol and water as solvent.

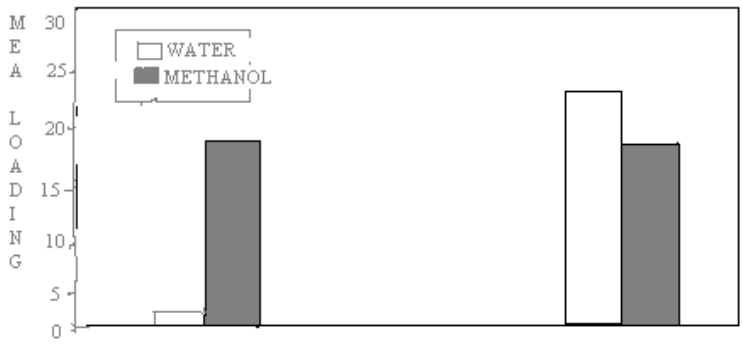


FIG-5 AGITATION PERIOD

EFFECT OF SOLVENT ON MEA LOADING

From the figure 5, it can be concluded that comparative MEA loadings can be achieved by using methanol in lesser time than water as solvent. From drying, it was observed that methanol immobilized adsorbents can be dried in lesser time as compared to their aqueous counterparts which can be attributed to high volatility of methanol. Thus, from these observations, we can infer that methanol is solvent of choice for the immobilization of MEA on the zeolite matrix (Chatti et al., 2009).

Effect of contact time on the amine loadings

It is clear from figure, that highest loading achieved in case of aqueous solvent with contact time of 4 h, whereas comparative loading was achieved with 15 min contact time using methanol as a solvent. Thus, we can infer that when methanol is used as solvent, lesser time is required to immobilize a comparative content of amine on the zeolite (Chatti et al., 2009).

Effect of wetting of the zeolite by methanol

For this study, two sets of experiment was planned. The first set of experiment was the immobilization of the amine onto the surface of the zeolite beads directly without any pretreatment. The second set of experiment was performed by initial wetting procedure of the zeolite beads with the solvent in a solid liquid ratio of 1:2 in two stages. Both the experiments were conducted at room temperature and agitation period was 15 min. It was observed that without any pretreatment there was not any significant loading. Whereas, for the prewetted

zeolite, the loading was observed to be 18.69%. Loading in pretreated zeolite was attributed to reaction of silanol and aluminol groups, present in zeolite, with methanol to form Si-O-CH_3 and water which in turn react with amine molecules to form highly reactive species (Chatti et al., 2009). Reactions are as follows:

Si-OH + CH_3OH ---------- Si-O-CH_3 + H_2O

Si-O-CH_3 + HO-CH_2-CH_2-NH_2 ---------- Si-O-CH_2-CH_2-CH_2-NH_2

By reflux with organic solvent solution of amine

The modification of zeolite was also done by refluxing the zeolite beads with respective amine solution with methanol at 70 ^{0}C. It is done to study the effect of temperature on amine loadings. In a typical modification procedure, 15 g of zeolite 13X beads were refluxed with 30 ml of alcoholic amine solution in a round bottom flask equipped with a water condenser. After 2 h reflux, the amine solution was decanted and the beads were allowed to dry in air over night (Chatti et al., 2009).

Effect of temperature in amine impregnation

Effect of temperature on impregnation was studied by conducting two sets of experiments. In both the experiments pretreatment was given to zeolite 13X beads by wetting the beads with solvent in solid liquid ratio of 1:2. The first experiment was conducted by immobilization of MEA on zeolite 13Xbeads at room temperature by using methanol as the solvent. The second experiment was carried out in a round bottom flask and the reaction mixture was refluxed at 70 ^{0}C. In both the experiments, concentration of alcoholic amine solution was 50 wt%. MEA loading observed in impregnation at room temperature is 18.63%, while at reflux method MEA loading was 13.88%. Thus it can be reflux method yield lower amine loading than simple mixing method (Chatti et al., 2009).

2.2 Combination of sodium carbonate and water as adsorbent.

The reversible reaction between sodium carbonate, CO_2 and H_2O, to form sodium bicarbonate can be used in thermal-swing process to recover concentrated CO_2 from power plant flue gases. This CO_2 capture process (Dry carbonate process) makes use of the well-known reaction chemistry of sodium carbonate (Na_2CO_3 or soda ash) and sodium bicarbonate ($NaHCO_3$ or baking soda). Sodium carbonate captures CO_2 in presence of water (H_2O) to form sodium

bicarbonate. Increasing the process temperature causes the bicarbonate to decompose and release a CO_2/steam mixture that can be converted into a pure sequestration ready CO_2 gas stream.

Reaction for CO_2 capture :

Na_2CO_3 (s) + CO_2 (g) + H_2O (g) ---------- 2$NaHCO_3$ (s) $\triangle H_r^0$ = -1325 Btu/lb CO_2

This reaction is highly exothermic. The equivalent reverse reaction is endothermic and produces an equal molar quantity of CO_2 and H_2O. Condensation of H_2O from the regeneration product results in a pure CO_2 stream suitable for sequestration or reuse (Nelson et al.).

2.3 Impregnation of potassium carbonate on solid support

Solid support chosen was activated carbon. Eight grams (8g) of activated carbon was prepared to form powder with the aid of a mortar and pestle and added to two grams (2g) of anhydrous K_2CO_3 in 7 ml of de-ionized water. The water was sufficient enough to form the hydrated complex of potassium carbonate. In the experimental set up, there was 20% loading of potassium carbonate onto the activated carbon powder. It was then mixed thoroughly with the aid of a stirrer. After stirring, some samples of potassium-based sorbents were air-dried (25 ^{0}C), some were dried in an oven at 60 ^{0}C, some were dried in an oven at 150 ^{0}C for different experimental runs. Reaction for CO_2 capture :

K_2CO_3*1.5H_2O + CO_2 ---------- 2$KHCO_3$ + .5H_2O + heat

2.4 Activation

Physical activation

Char was obtained from Raw almond shells as in case of amination. Resulting char(A) was subjected to physical activation. Activation with CO_2 was conducted at 800 ^{0}C to different degrees of burn-off. When duration of treatment is 2 h, the modified sample is indicated as AA2 and when duration of treartment is 3 h, the modified sample is indicated as AA3 (Plaza et al., 2009).

Characterization

Samples were characterized in terms of texture, chemical composition and surface chemistry. The textural characterization was carried out by determining the N_2 and CO_2 adsorption at -196 ^{0}C and 0 ^{0}C respectively. pH of a suspension containing 0.25 g of sample in 1.5 cm^3 of distilled water was measured once the equilibrium was reached under inert atmosphere. Temperature desorption tests were carried out in a thermogravimetric analyser which was coupled to Fourier

Transform Infrared spectrometer via a heated interface to analyse the evolved gases. The CO_2 capture performance of prepared adsorbents was evaluated by means of a thermobalance Setaram TGA 92, which recorded mass uptake of the samples when exposed to CO_2.

Results of characterization

AA2 showed pH of 10.4, volatile matter content of 5.8, ash content of 5.3, carbon content C 91.1%; nitrogen content N 0.9%, hydrogen content H 0.7%, oxygen content O 7.3%. AA3 showed pH of 11.0, volatile matter content of 6.0%, ash content of 6.3%; carbon content C 90.6%, hydrogen content H 0.6%, nitrogen content N 0.9%, oxygen content O 7.9%. Thus it can be inferred that longer time of treatment of activation gives lower percentage of carbon, hydrogen, but higher percentage of oxygen. Temperature desorption tests on AA2 showed release of CO at high temperature indicating the formation of basic pyrrone functionalities during the activation process. Activation leads to higher value of BET surface area, total pore volume, narrow micropore volume, micropore surface area, but narrow micropore width is not higher. It can also be inferred that longer time of treatment leads to higher value of all the textural parameters. Adsorption capacity is higher for activated sample than the unactivated sample. Also longer time of treatment gives slightly higher adsorption capacity.

Chemical activation

In "chemical activation" the precursor is mixed with a reagent that participates in and so modifies the chemical reactions that occur during subsequent heat treatment. The most commonly used reagent in chemical activation is phosphoric acid, H_3PO_4. Activation of a wide range of precursors with potassium hydroxide, KOH, has been studied in laboratory.

2.5 Impregnation of Fe_2O_3 and Cr_2O_3 promoted by Zinc on solid support

Solid support chosen is activated carbon. The surface chemistry of the activated carbons can be efficiently modified by chemical impregnation which together with the intrinsic nature of the activated carbon can highly increase the adsorption capacity (Manocha, 2003). According to the nature of adsorbate, the surface chemistry of activated carbon can be modified by creating acidic or basic groups (Sun et al., 2007). As CO_2 is an acidic gas, the presence of basic species can cause a prior basic character of carbon surface which promotes the CO_2 capture capacity (Alvim-Ferraz and Todo-Born, 2003; Lach et al., 2007). Metal oxides chosen for impregnation are Fe_2O_3 and Cr_2O. Promoting agent is Zn^{2+}.

Surface treatment (Preparation of metal oxide/AC samples)

The raw activated carbon was refluxed several times with distilled water before impregnation in order to remove unwanted alkali components and impurities (Kaluza and Drazil, 2001). Impregnation was carried out at room temperature by immersing 0.001 kg of raw activated carbon in aqueous suspension of metal oxides for 5 days. The mixture was containing 0.6-0.7 kg metal oxide per kg of activated carbon. Sample was named as name of metal oxide (T,I) where T is temperature and I represents slurry or solution (Somy et. al., 2008). In order to investigate the effect of washing stage on the adsorption properties of CO_2 on impregnated activated carbons two other samples were prepared with or without washing before drying in a rotary vacuum evaporator. Prepared samples were named as Fe_2O_3 (25, Slurry), Cr_2O (25, Slurry), Fe_2O_3 (25, Slurry)-washed and Cr_2O (25, Slurry)-washed.

Preparation of Zn^{2+}-metal oxide sample

Two different methods of deposition of zinc on activated carbon impregnated by metal oxides (in previous section). One method is by aqueous solution method other method is by aqueous slurry method. Aqueous solution is the solution of zinc nitrate. Aqueous slurry is the slurry of zinc hydroxide carbonate. The aqueous solution of zinc nitrate was prepared by dissolving 0.1 kg of zinc nitrate hexahydrate in 0.001 m^3 of de-ionized water. Mass of zinc hydroxide carbonate powder used in preparation of slurry was calculated according to 2 wt% of loading purpose. In solution impregnation method, activated carbon loaded with metal oxides were left with zinc nitrate solution for 1-2 h with occasional gentle shaking while in slurry impregnation method samples were left in the aqueous slurry of zinc hydroxide carbonate for 5 days. The mixtures were dried in rotary vacuum evaporator for 30-60 min at 85-95 ^{0}C (Somy et. al., 2008).

Characterization

BET surface area of sample was measured by N_2 adsorption-desorption isotherms at 77 K in an automatic adsorption system.

Results of characterization

Table 1 BET surface area of the activated samples

Sample	S_{BET} (m^2/g)	Relative drop in BET (%)
Activated carbon	959	-----
Fe_2O_3 (25, Slurry)-washed	951	0.83
Cr_2O (25, Slurry)-washed	927	3.3
Zn-Cr_2O (25, Slurry)	814	15
Zn-Cr_2O (25, Solution)	795	17
Zn-Cr_2O (95, Solution)	541	43

As presented in table1, the samples prepared by slurry impregnation lead to larger surface area than solution prepared by solution impregnation method.

CO_2 adsorption studies

CO_2 adsorption tests were carried out volumetrically in a stainless steel vacuum system. Using the volumetric method with P-V-T measurements, the total amount of gas introduced into the system and the gas remaining in the system after reaching adsorption equilibrium was determined. The adsorbed amount was calculated using ideal gas law at low pressure prevailing, by measuring the pressure drop caused by CO_2 adsorption.

Effect of surface treatment method on CO_2 adsorption capacity of impregnated Activated Carbon

CO_2 adsorption capacity of activated carbons modified by slurry impregnation method is more than those modified by solution impregnation method. Decrease in adsorption capacity by solution impregnation method can be explained due to pore blocking in the structure of activated carbon after dipping of activated carbon in a solution of additives (Bansal and Goyal, 2005, Bowker et al., 2007, Przepiorski et al., 2004). It seems that using slurry impregnation method prevent blocking of the pores during impregnation. It is also suggested that distribution of impregnate species on activated carbon is better by slurry impregnation method. Sample

impregnated with Fe_2O_3 showed more decrease in adsorption capacity. The reason for this observation may be due to large molecular size of Fe_2O_3 that leads to improper distribution of Fe_2O_3 agent on activated carbon surface. It may also cause blocking of micropores which can result in decrease in adsorption capacity. Table 1 shows that surface area decreased using both the impregnation method although decrease was negligible for slurry washed impregnation method. Decrease in surface area may be attributed to distribution of impregnating species in pores of adsorbents. The impregnation temperature also affect the structural properties of activated carbon such as surface area that can be seen in table 1.

Effect of impregnation temperature on CO_2 adsorption capacity of impregnated activated carbon

Adsorption volume of CO_2 on impregnated activated carbon related to the higher impregnation temperature was much lower than volume adsorbed on activated carbon impregnated at lower temperature. Chemical impregnation is basically considered as chemical reaction between the solid adsorbent and the chemical impregnating agent. It is expected that temperature affects the extent of chemical reaction and as result impregnation (Carabineiro et al., 2003).

Chapter-3

Materials and Methods

3.1 Materials

3.1.1 MEA (Monoethanolamine)

Analytical grade monoethanolamine (Molecular weight = 46, Density = 1.09-1.11g/l, 99.9% pure) procured from S. D. Fine Chemicals Ltd. India.

3.1.2 Zeolite13X

Zeolite 13X which is a complex of Sodium oxide, Alumina and Sillicate in form of pellets of 1.5 mm was procured from Merck specialities Pvt. Ltd. India.

3.1.3 Perchloric acid

Perchloric acid (Molecular weight = 100.5) used for titrimetic analysis for determination of amine loading on Zeolite was procured from S. D .Fine Chemicals Ltd. India.

3.1.4 Acetic Anhydride

Acetic Anhydride (Molecular weight = 102) used in titrimetric analysis for determination of amine loading on Zeolite was procured from S. D. Fine Chemicals Ltd. India.

3.1.5 Glacial Acetic acid

Glacial acetic acid (Molecular weight = 60) used in titrimetric analysis for determination of amine loading on Zeolite was procured from Qualigens Fine Chemicals Ltd. India

3.1.6 Methyl Orange

Methyl Orange used as indicator in titrimetric analysis for determination of amine loading on Zeolite was procured from Central drug house.

3.1.7 Xylene Cyanol

Xylene Cyanol used as indicator in titrimetric analysis for determination of amine loading on Zeolite was procured from Loba chemie.

3.1.8 Crystal Violet

Crystal Violet used as indicator in titrimetric analysis for determination of amine loading was procured from Merck specialities Pvt. Ltd.

3.2 Methodology

Immobilization of amine on adsorbents was carried out by preparing the solution of MEA in aqueous media. Five different concentrations of 0 wt %, 5 wt %, 10 wt %, 15 wt % and 20 wt% MEA were prepared. Zeolite13X was crushed to make fine powder.These solutions were mixed with powdered Zeolite13X keeping solid liquid ratio of 1:2. They were kept in a rotary shaker for 4 hrs at rpm of 130 and room temperature(26 ^{0}C). After shaking, solid liquid were separated by decantation and centrifugation. Zeolite was air dried and liquid solution was used for titrimetric analysis.

1.) 5 wt % MEA solution was prepared as follows :

Volume of water taken = 47.5 ml

Volume of MEA(99.9%) taken = 2.5 ml

2.)10 wt % MEA solution was prepared as follows :

Volume of water added = 45 ml

Volume of MEA(99.9%) added = 5 ml

3.)15 wt % aqueous MEA solution was prepared as follows :

Volume of water taken = 42.5 ml

Volume of MEA(99.9%) taken = 7.5 ml

4.)20 wt % aqueous MEA solution was prepared as follows :

Volume of water taken = 40 ml

Volume of MEA(99.9%) taken = 10 ml

3.3 Analytical/Testing Procedures

3.3.1 Standardisation of Perchloric acid

Preparation of perchloric acid – 900 gm of glacial acetic acid is added into a dark coloured bottle, 142 ml of perchloric acid (70%) is added and shaken well. 38 ml of acetic acid is added in small amount and mixed well. 0.5 gm of potassium hydrogen phthalate is added into clean and dry conical flask. 50 cc of glacial acetic acid is added into flask. 2-3 drops of crystal violet indicator is added. Solution in flask is titrated against perchloric acid to bluish-green end point. Normality of perchloric acid is calculated via this standardisation.

3.3.2 Determination of concentration of amine

10 ml of initial MEA solution is taken in 250 ml of conical flask. It is mixed with glacial acetic acid. 2-3 drops of methyl orange and 2-3 drops of Xylene cyanol is added. It is then titrated with perchloric acid to pink end point. Same titration is done with residual MEA solution.

3.3.3 Fourier transform infrared (FTIR)

FTIR analysis is a useful tool to determine the formation of new or disappearance of functional groups. So chemical bonding on the surface of modified adsorbent was determined using this technique. A total of 6 scans were taken with a resolution of 4 cm^{-1}.

3.3.4 Adsorption Column set up

Adsorption column set up was obtained from Chemito Technologies Pvt. ltd., Mumbai, India. It consists of four sections. Gas feeding section, Reactor section, Outlet section, Microprocessor based control panel section. In gas feeding section, Nitrogen gas and Carbon Dioxide gas is allowed to enter separately in the Pre-mixer with controlled flow rate through Mass flow controller. Inlet pressure is sensed by pressure gauge. Non return valve / check valve is used to prevent back flow. In reactor section, Fixed bed reactor is operated in downflow direction. Gas

mixture is entered through top of the reactor. Furnace of reactor is split type heating furnace with single zone and can be controlled independently based on the skin temperatures. Pressure of system is sensed by pressure gauge and pressure transmitter. In outlet section, outlet gases fromthe reactor section is sent to gas chromatography for further analysis

3.3.5 Calculation of determination of amine loading

0.5/204.22 = N * Volume of perchloric acid used in standardisation

N is normality of perchloric acid used in titration.

N* Volume of perchloric acid used = N_1*10(Volume of initial solution taken)

N_1 is normality of initial solution taken.

N* Volume of perchloric acid used = N_2*(Volume of residual solution taken)

N_2 is normality of residual solution taken.

Mass of amine loaded on Zeolite = (N_1-N_2)*61.08/100 per 5 gm of Zeolite

CHAPTER – 4

RESULTS AND DISCUSSION

CALCULATIONS

1.)Standardisation :

In Flask : 0.5 gm of Potassium Hydrogen phthalate + 50 cc of Glacial Acetic acid + Crystal Violet Indicator

In Burette : N / 10 Perchloric Acid

End point : Bluish to green point

Volume of Perchloric Acid used = 17 ml

No. of gram equivalents = N*V

0.5/204.22 = N*17/1000 [No. of gram equivalents = 0.5/204.22, V = 17 ml]

N = 0.144

Initial aqueous MEA solution :

In Burette : Volume of perchloric acid used = 50 ml, N = 0.144

In Flask : Volume of MEA solution = 10 ml, N= ?

N = 0.72 (N = No. of gram equivalents / Volume of solution in liter)

Mass = 0.72*61.08 /100 = 0.4397 gm of MEA in 10 ml of solution (0.8794 gm per 20 ml of MEA solution)(10 gm of Zeolite 13X)

Filterate(Residual MEA solution) :

In Burette : Volume of Perchloric acid used = 17.5 ml, N = 0.144

In Flask : Volume of MEA solution = 10 ml, N = ?

N = 0.252

Mass = 0.252*61.08/100 = 0.1539 gm of MEA in 10 ml of solution (0.3078 gm per 20 ml of solution)(10 gm of Zeolite 13X)

Loading = 0.8794 -0.3078 = 0.5716 of MEA added per 10 gm of Zeolite

2.)Standardisation :

In Flask : 0.5 gm of Potassium Hydrogen phthalate + 50 cc of Glacial Acetic acid + Crystal Violet Indicator

In Burette : N / 10 Perchloric Acid

Volume of Perchloric acid used = 17.8 ml

0.5/204.22 = N*17.8/100

N = 0.138

Initial aqueous MEA solution :

In Burette : Volume of Perchloric acid used = 94 ml, N = 0.138

In Flask : Volume of MEA solution = 10 ml, N = ?

N = 1.2972

Mass = 1.2792*61.08/100 = 0.7923 gm in 10 ml of MEA solution (1.5843 gm in 20 ml of solution)(10 gm of Zeolite 13X).

Filterate(Residual MEA solution) :

In Burette : Volume of Perchloric acid used = 72 ml, N = 0.138

In Flask : Volume of MEA solution = 10 ml, N = ?

N = 0.9936

Mass = .9936*61.08/100 = 0.6068 gm in 10 ml of MEA solution (1.2136 in 20 ml of MEA solution)(10 gm of Zeolite13X).

Loading = 1.5846 – 1.2136 = 0.3710 gm of MEA added per 10 gm of Zeolite13X.

3.)From standardisation , N = 0.144

Initial aqueous MEA solution :

In Burette : Volume of Perchloric acid used = 126 ml, N = 0.144

In Flask: Volume of MEA solution = 8 ml, N = ?

N = 2.268

Mass = 2.268*61.08/100 = 1.385 gm of MEA in 10 ml of solution(2.77 gm of MEA in 20 ml of solution)(10 gm of Zeolite 13X)

Filterate(Residual MEA solution) :

In Burette : Volume of Perchloric acid used = 51 ml, N = 0.144

In Flask : Volume of MEA solution = 10 ml, N = ?

N = 0.7344

Mass = 0.7344*61.08/100 = 0.4486 gm in 10 ml of solution(0.8972 gm in 20 ml of solution)(10 gm of Zeolite 13X)

Loading = 2.77 – 0.8972 = 1.8728 gm of MEA loaded per 10 gm of Zeolite 13X.

4.)From standardisation, N = 0.153

Initial aqueous MEA solution :

In Burette : Volume of Perchloric acid used = 198 ml, N = 0.153

In Flask : Volume of MEA solution = 10 ml, N = ?

N = 3.0294

Mass = 3.0294 *61.08/100 = 1.8503 gm in 10 ml of solution (3.7007 in 20 ml of solution)(10 gm of Zeolite 13X).

Filterate (Residual MEA solution) :

In Burette : Volume of Perchloric acid used = 69 ml , N = 0.153

In Flask : Volume of MEA solution = 10 ml, N = ?

N = 1.0557

Mass = 1.0557*61.08/100 = 0.6448 gm of MEA in 10 ml of solution(1.2896 gm of MEA in 20 ml of solution)(10 gm 0f Zeolite 13X).

Loading = 3.7007 – 1.2896 = 2.4111 gm of MEA loaded per 10 gm of Zeolite 13X

4.1 Amount of Amine loaded on Zeolite 13X

Table 2

Concentration	MEA in initial soln. per 20 ml of solution (gm).	MEA in final soln. per 20 ml of solution (gm).	Loading per 10 g of Zeolite 13X	% age in Zeolite 13X
5 wt % MEA	0.8794	0.3708	0.5716	5.716
10 wt% MEA	1.5846	1.2136	0.3710	3.710
15 wt% MEA	2.77	0.8972	1.8728	18.728
20wt % MEA	3.7007	1.2896	2.4111	24.111

Out of four modifying solution of 5 wt %, 10 wt%, 15 wt% and 20 wt% MEA prepared, percentage of MEA loaded was maximum in case of 20 wt % MEA solution. In literature, 2 wt % MEA modified Zeolite 13X, gave loading of 0.5%. 5 wt% MEA modified Zeolite13X gave loading of 5.716% which is comparatively higher. In our work,10 wt% MEA modified Zeolite gave loading of 3.710% which is comparable to that given in literature which showed loading of 2.9% for 10 wt% MEA modified Zeolite13X. In literature, 25 wt% MEA modified Zeolite 13X gave loading of 13.53%, while in our work 15 wt% and 20 wt% MEA modified Zeolite 13X gave loading of 18.728% and 24.111% respectively, which are comparatively higher.

Optimal MEA loading equivalent to pore filling is 23.28% so loading of 24.111% in case of 20 wt% MEA modified Zeolite 13X seems not possible, but higher loading is also reported in literature as in case of 80 wt% MEA modified Zeolite 13X which showed loading of 28.75% through titrimetry analysis.

4.2 FTIR Spectra of Zeolites

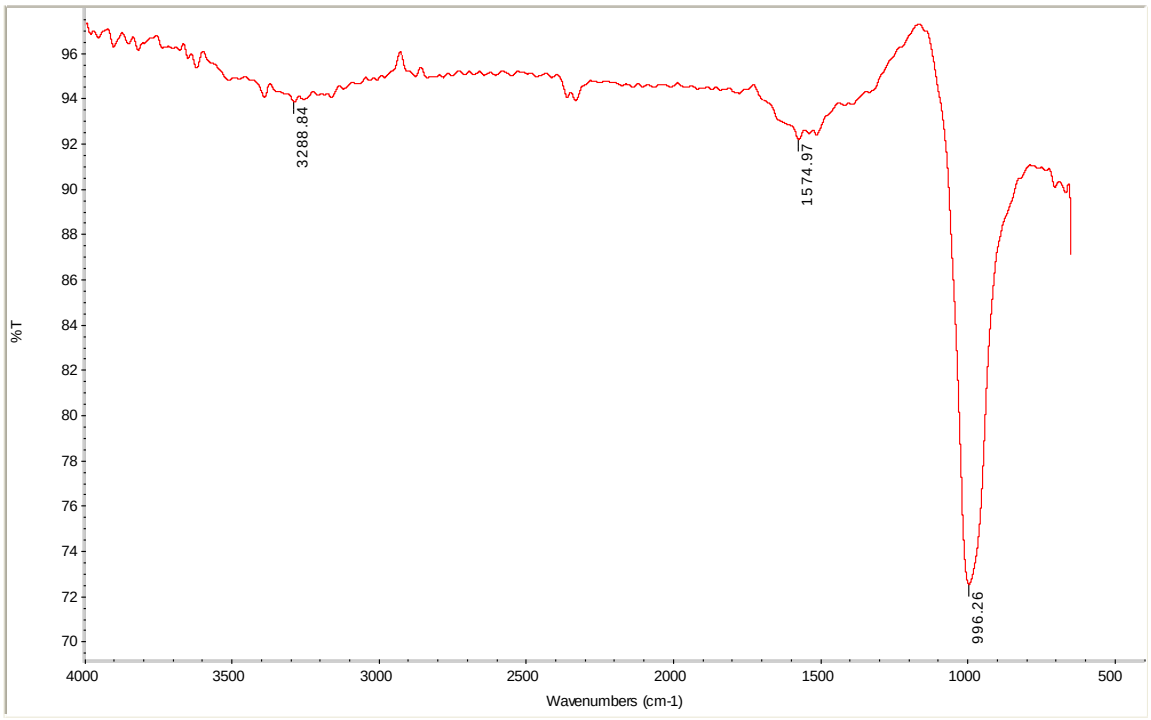


Fig- 7,10 wt% MEA modified Zeolite 13X (Loading unanalysed)

There is a peak observed at about 1000 cm^{-1}, which indicates the presence of C-N bonding and consequently the amine group in modified Zeolite 13X.

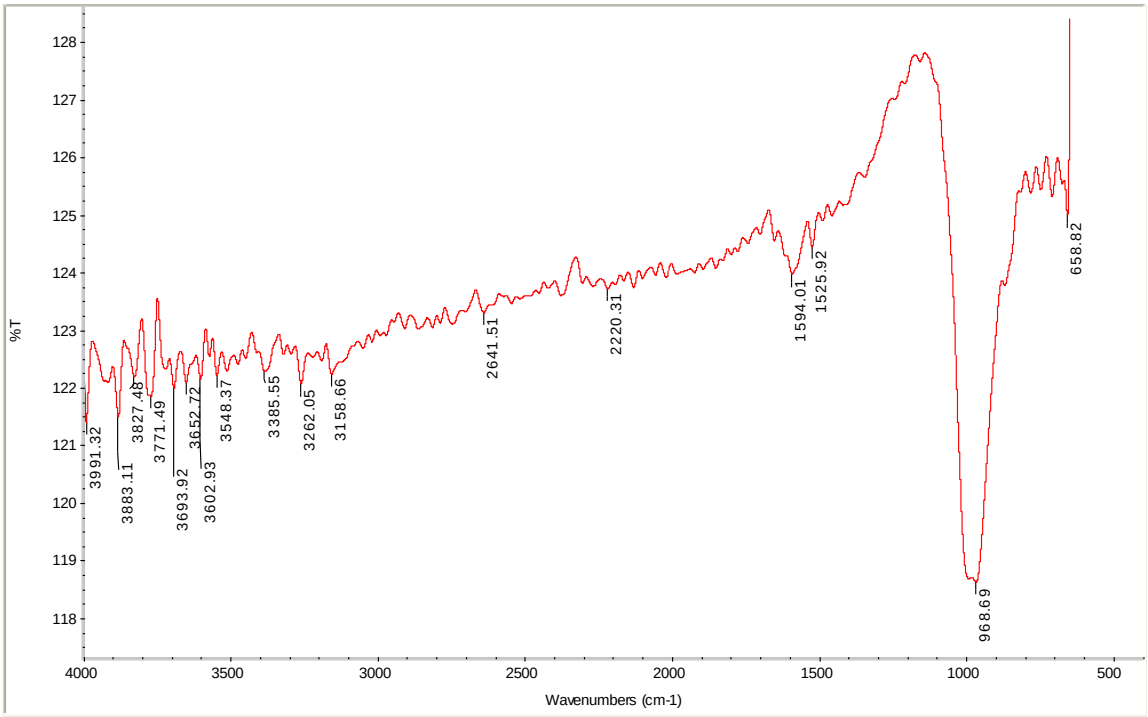


Fig-8,10 wt% MEA modified Zeolite 13X

There is a peak observed at about 1000 cm^{-1}, which indicates the presence of C-N bonds and the presence of amine group in modified Zeolite13X. Also large intensity corresponding to peak verify the loading of 3.716% on Zeolite 13X.

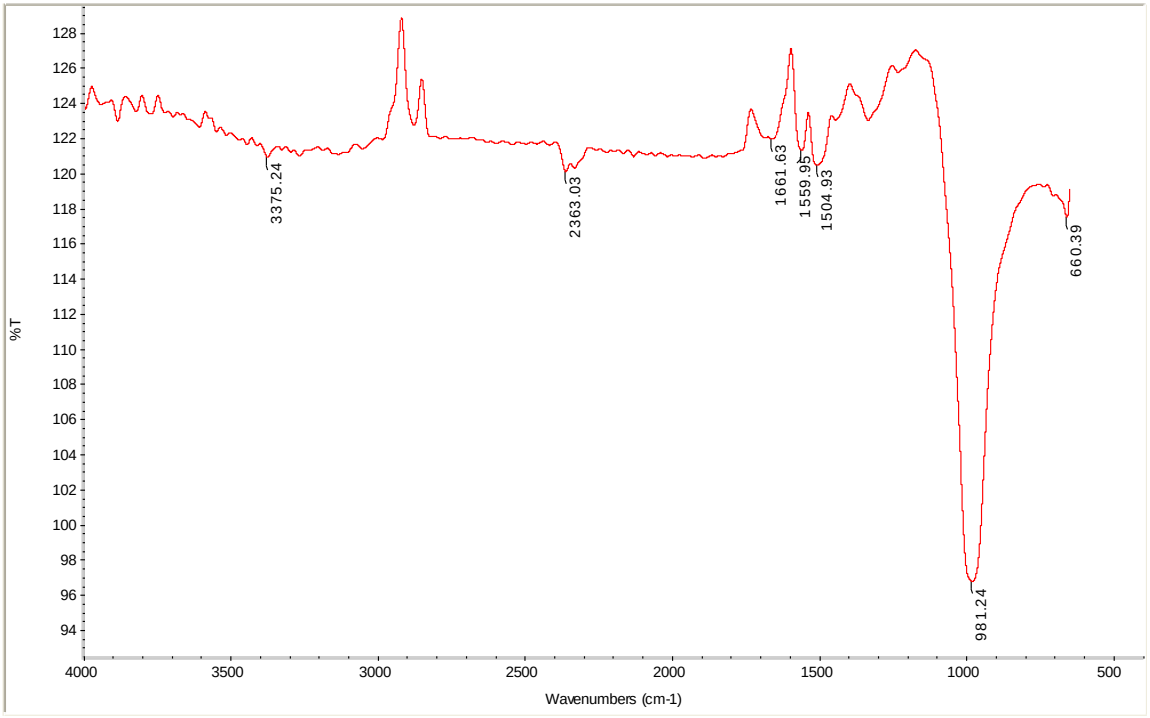


Fig-9,15 wt% MEA modified Zeolite 13X

There is a peak observed at about 1000 cm^{-1}, which indicates the presence of C-N bonds and the presence of amine group in modified Zeolite13X. Also large intensity corresponding to peak verify the loading of 18.7% on Zeolite 13X.

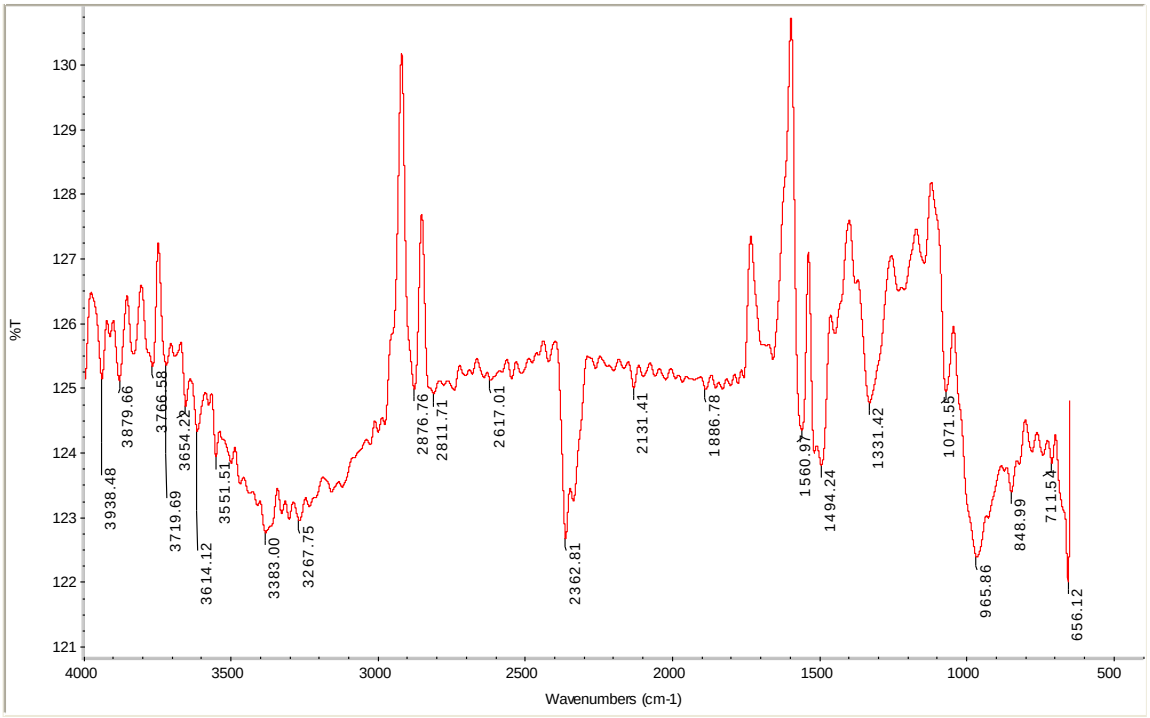


Fig-10,20 wt% MEA modified Zeolite 13X

There is a peak observed at about 1000 cm^{-1}, which indicates the presence of C-N bonds and the presence of amine group in modified Zeolite13X. Presence of peak at 2362.81 cm^{-1}, indicates the presence of C-H bonding in modified Zeolite 13X. Intensity of peak corresponding to C-N bonding is little lower as compared to other samples.

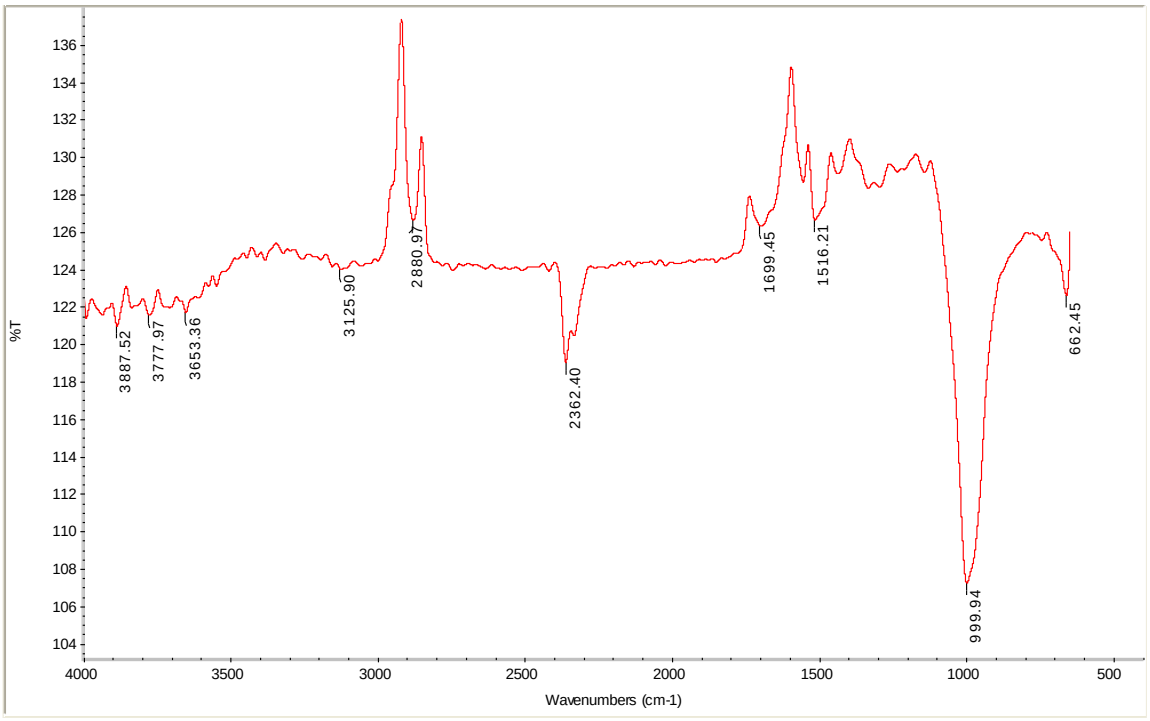


Fig-11,5 wt% MEA modified Zeolite 13X

There is a peak observed at about 1000 cm^{-1}, which indicates the presence of C-N bonds and the presence of amine group in modified Zeolite13X. Also large intensity corresponding to peak verify the loading of 5.716% on Zeolite 13X.

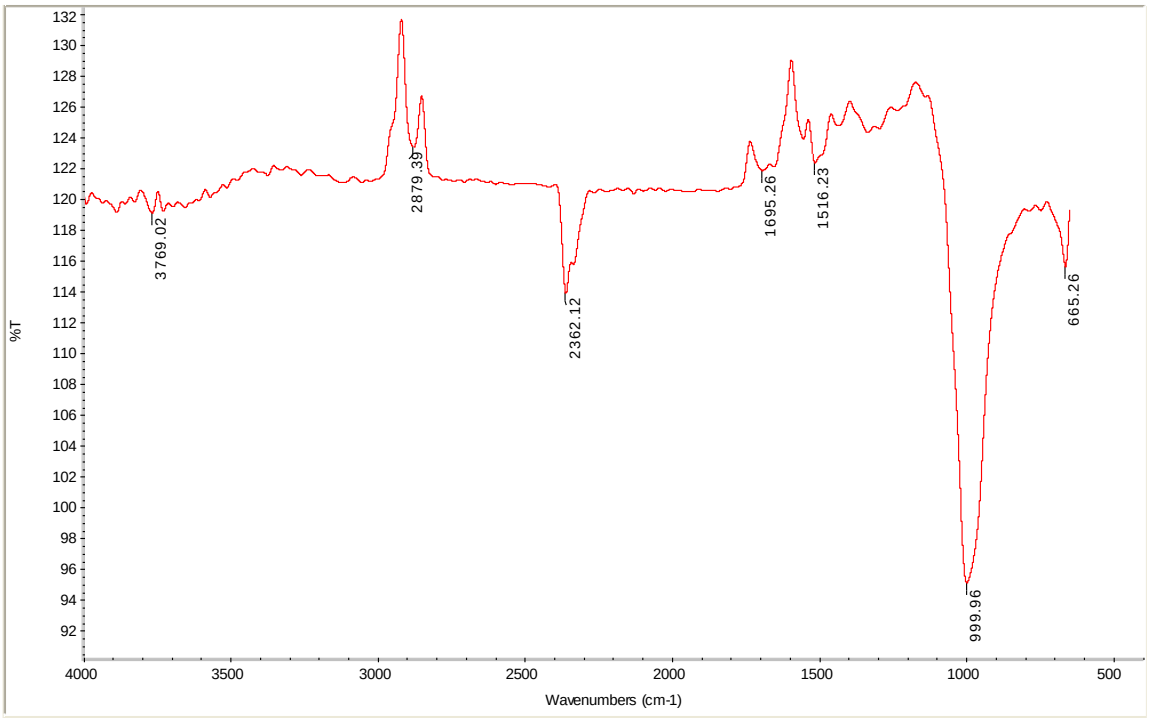


Fig-12, Pure water modified Zeolite

4.3 Breakthrough curve of bare Zeolite and modified Zeolite as obtained by adsorption column set up.

Operating conditions:

Adsorption temperature – 30 ^{o}C

Gas flow rate for CO_2 – 4 ml/min

Gas flow rate for N_2 – 22 ml/min

N_2, CO_2 Conc. both in volume %

Table 3 Bare Zeolite

Time	N_2 Conc.	CO_2 Conc.	C/Co for CO_2
7.5	59.05767	0.615141	0.053614
14.5	50.35116	11.8131	1.029606
21.5	50.02884	12.09864	1.0543366
28.5	49.80082	12.25153	1.067818
35.5	49.59516	12.32585	1.074296
42.5	49.46413	12.42354	1.082811
49.5	49.5158	12.31655	1.074385
56.5	49.23892	12.41344	1.08193
63.5	49.24967	12.35772	1.077074
77.5	49.11836	12.3816	1.079155

Table 4 Zeolite (20% MEA modified)

Time	N_2 Conc.	CO_2 Conc.	C/Co for CO_2
0.5	50.44153	10.59044	0.86013429
5.5	48.7284	12.37383	1.004977648
10.5	48.56682	12.49123	1.008664945
15.5	48.54652	12.43751	1.01014961
20.5	48.55311	12.51393	1.016356289
25.5	48.67729	12.54286	1.018705925
30.5	48.75952	12.61186	1.024309967
35.5	48.87501	12.62549	1.025416968
40.5	49.13542	12.72216	1.033268313
45.5	49.51514	12.83085	1.042095895
55.5	50.02292	12.02433	1.057809953
60.5	47.73231	12.41034	1.00794217

Where C is concentration of CO2 in gas going to the adsorption column

Where Co is concentration of CO2 in Zeolite

Fig-13 Breakthrough curve of bare Zeolite.

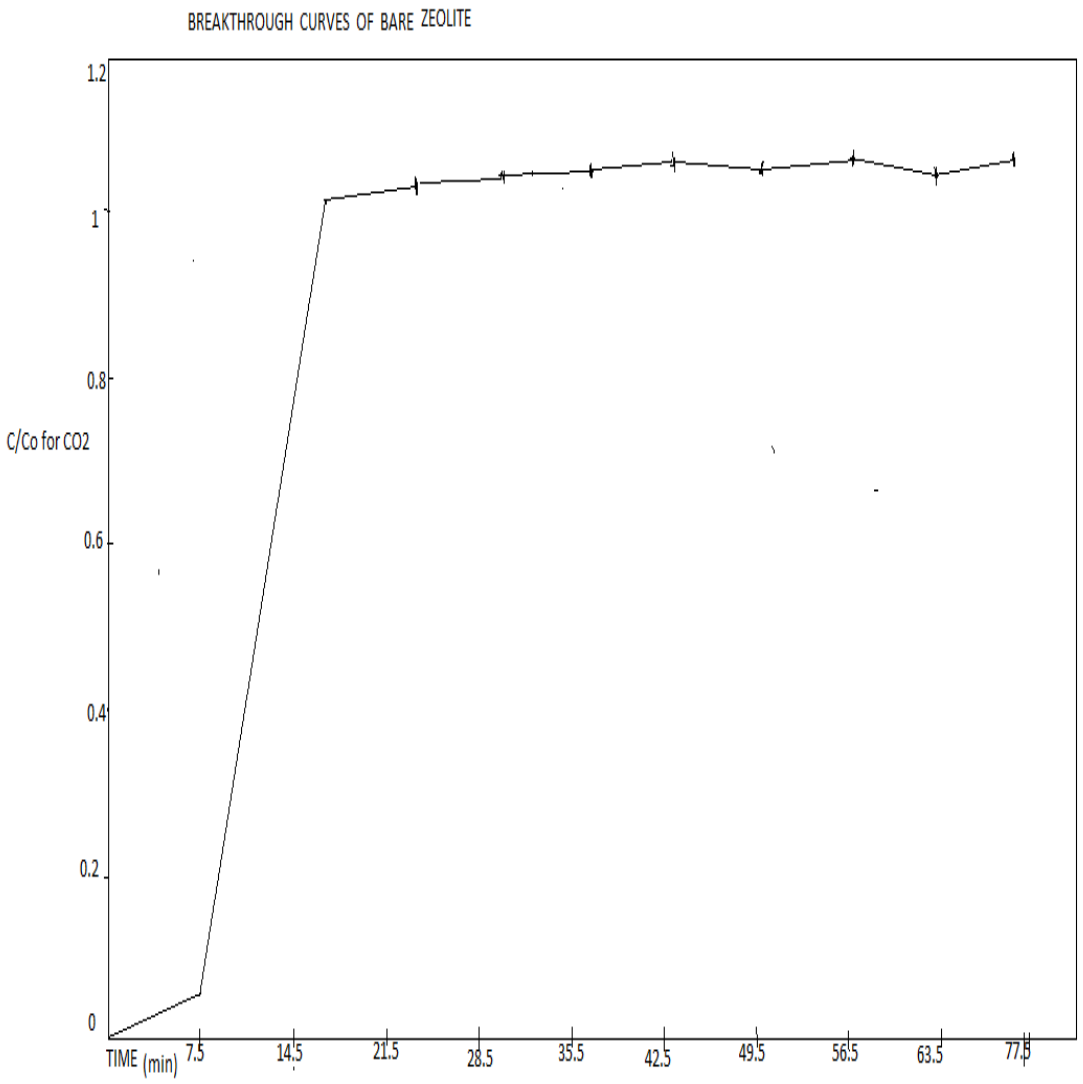
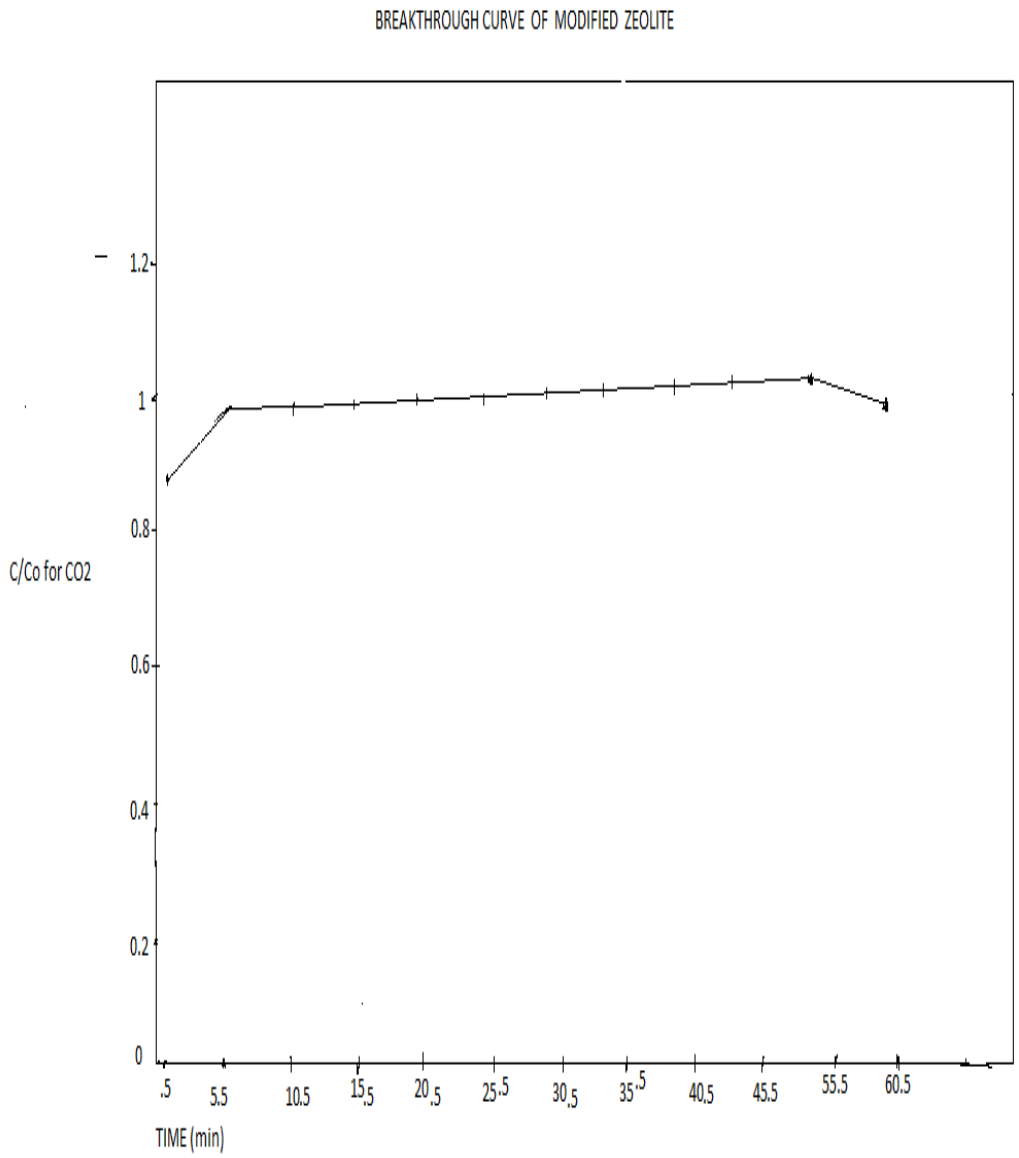


Fig 14 Breakthrough curve of modified Zeolite



From the curve it seems that though CO_2 adsorption has taken place, samples were not completely activated so quantitative analysis of adsorption capacity from these curves could not be made.

CHAPTER – 5

CONCLUSION

Loading of MEA on Zeolite13X as analysed by titrimetry analysis comes out to be appreciable even higher than that shown by literature. In case of 20 wt% MEA modified loading has come out to be higher than optimal loading equivalent to pore filling. It might have resulted in pore blocking. FTIR spectra of all the modified Zeolite13X has a peak at 1000 cm^{-1} which is indicative of C-N bond thus the loading of MEA has been successfully done on all the Zeolite 13X. Intensity corresponding to peak are also higher except in case of 20 wt% MEA modified Zeolite 13X which is indicative of higher MEA loading on Zeolite 13X except in case of 20 wt% MEA modified Zeolite 13X. This FTIR spectra of 20 wt% MEA modified Zeolite 13X contradicts the titrimetry analysis done in this case. FTIR spectra behaviour in case of 20 wt% MEA modified is not understood. Breakthrough curve was obtained from experiment done on bare Zeolite and modified Zeolite in adsorption column set up. Samples seemed to be not completely activated so quantitative analysis of adsorption capacity from these curves could not be made, although adsorption of CO_2 has taken place.

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