

Technoeconomic Investigation of Amine-Grafted Zeolites and Their Kinetics for CO₂ Capture

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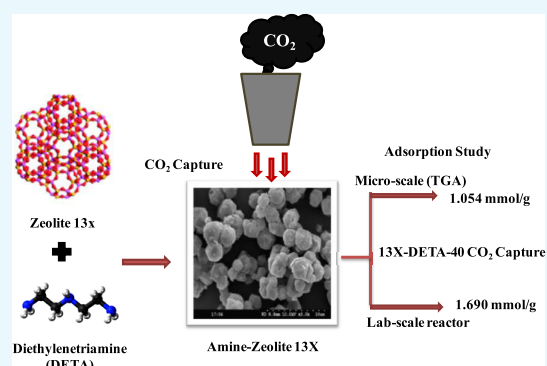


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ABSTRACT: Solid adsorbents with precise surface structural chemistry and porosity are of immense interest to decode the structure–property relationships and maintain an energy-intensive path while achieving high activity and durability. In this work, we reported a series of amine-modified zeolites and their CO₂ capture efficiencies. The amine impregnated molecular zeolite compounds were characterized and systematically investigated for CO₂ adsorption capacity through thermogravimetric analysis for the occurrence of atmospheric pure CO₂ gas at 75 °C with diethylenetriamine (DETA), ethylenediamine (EDA), monoethanolamine (MEA), and triethanolamine (TEA)-loaded zeolite 13X, 4A, and 5A adsorbents. The kinetics of the adsorption study indicated that the adsorption capacity for CO₂ adsorption was improved with amine loading up to a certain concentration over 13X-DETA-40, showing an adsorption capacity of 1.054 mmol of CO₂ per gram of zeolite in a very short amount of time. The result was especially promising in terms of the initial adsorption capacity of zeolite, which adsorbed approximately 0.8 mmol/g zeolite within the first two minutes of experimentation. A detailed flow chart that includes a brief look into the process adopted for adsorption was included. Lagergren pseudo-first- and pseudo-second-order models of 40 wt % DETA zeolite 13X gave CO₂ adsorption capacities of 1.055 and 1.058 mmol/g and also activation energies of 86 and 76 kJ/mol, respectively. The CO₂ adsorption capacity of 13X-DETA-40 in a lab-scale reactor was found to be 1.69 mmol/g. A technoeconomic study was conducted for the solid amine zeolites to understand the investment per ton of CO₂ adsorbed. This study was used as a basis to improve cost estimates from a microscale to a lab-scale reactor. The cost of investment for 13X-DETA-40 was reduced by 84% from \$49,830/ton CO₂ adsorbed in a microscale reactor to \$7,690/ton of CO₂ adsorbed in a lab-scale reactor.



1. INTRODUCTION

Global warming has been considered to be one of the significant environmental problems in the present scenario, which tends to deplete the ozone layer. CO₂ is considered as one of the greenhouse emission gases that are majorly liberated from fossil fuel plants.^{1,2} The development of different carbon capture and storage (CCS) technologies to rationalize the generation of CO₂ from the fossil fuel plants into the atmosphere has been a significant concern to sequester CO₂.³ Various technologies developed so far for CO₂ capture involve absorption, membrane technology, cryogenic CO₂ capture, and adsorption–desorption kinetics. Pressure swing adsorption kinetics is found to be the most prominent method for adsorption.^{4,5} The conventional approach of absorption through liquid amines possesses drawbacks of corrosion, incompetent regeneration kinetics, energy loss, and high cost values.⁶ To overcome these limitations, solid adsorbents have been found to possess various advantages such as superior adsorption capacities, high material stability, and high uptake efficiency under humid conditions.^{7–10} The studies on amine-modified adsorbents have gained significant attention in the

CO₂ capture research area because of their simple chemistry involved between the acidic CO₂ molecule and primary amine molecule impregnated on the zeolite surface. The different kinds of adsorbents used so far for CO₂ uptake or adsorption include zeolites,¹¹ porous amine-silica hybrid adsorbents,¹² metal-organic frameworks (MOFs),¹³ COFs, activated carbon,^{14,15} and alkaline metal oxide.^{16,17} Zeolites being highly stable possess higher porosity and adsorption kinetics. Different amine-based CO₂ capture processes are reported in the literature including different amines such as monoethanolamine (MEA),¹⁸ polyethylenimine (PEI),¹⁹ diethanolamine (DEA), 2-amino-2-methyl-1-propanol (AMP), isopropanolamine, etc. Bezerra et al. reported that ZX10 using MEA showed a higher CO₂ adsorption capacity at 348 K, resulting in

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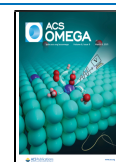


Table 1. Kinetic Models of Adsorption

kinetic model	nonlinear equation	linear equation	plot	slope and intercept
pseudo-first order	$\frac{dq_t}{dt} = k_1(q_e - q_t)$	$\log(q_e - q_t) = \log(q_e) - \left(\frac{k_1}{2.303}\right)t$	$\log(q_e - q_t)$ vs t	slope = $\frac{k_1}{2.303}$ intercept = $\log(q_e)$
pseudo-second order	$\frac{dq_t}{dt} = k_2(q_e - q_t)^2$	$\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{t}{q_e}$	$\frac{t}{q_t}$ vs t	slope = $\frac{1}{q_e}$ intercept = $\frac{1}{k_2q_e^2}$

1.10 mol/g CO₂ adsorption.¹⁸ Karka et al. demonstrated that 13X-PEI_{600000MW} shows 1.22 mmol/g CO₂ adsorption at an amine loading percentage of 60% at 75 °C.¹⁹ Jadhav et al. determined the adsorption capacities of MEA-modified zeolite 13X for a temperature variation of 30–120 °C, determining the incremental adsorption capacities with 1.6 and 3.5 CO₂ capture efficiencies at 30 and 120 °C, respectively.²⁰ Chen et al. reported that PEI_{800MW} with a silica-supported zeolite moiety shows 202 mg of CO₂ adsorption at 105 °C under a pure CO₂ atmosphere.²¹ The synthesized amine-loaded modified zeolites play a significant role in industrial applications; are majorly useful in renewable energy fields, fossil fuel plants to control the CO₂ emission, paper industry, steel plant, biomass conversion, thermal energy storage systems, and fuel cells; and are of great industrial importance. The current study mainly explores the adsorption kinetics of different amines such as diethylenetriamine (DETA), ethylenediamine (EDA), MEA, and triethanolamine (TEA) impregnated over different zeolites such as 13X, 4A, and 5A zeolites, respectively. The results obtained indicate a need to study zeolites 13X and 13X-DETA-40 further in a lab-scale reactor and perform process optimization specifically with 13X-DETA-40 to obtain a novel and cost-effective method of CO₂ adsorption.

2. CHARACTERIZATION

Various characterization techniques were considered to find a fair comparison between unmodified and amine-modified zeolite 13X. Various characterization techniques such as scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray powder diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), N₂ adsorption/desorption isotherms, thermogravimetric analysis (TGA), and elemental (CHNS) analysis have been carried out in the present study to depict the advantages and confirm the adsorption capacities of the as-synthesized modified zeolites.

The thermal stability of the sorbents has been analyzed using the TA Instruments SDT Q600 apparatus. The typical procedure includes the sample loading of approximately 20 mg in the TG pan with a heating rate of 10 °C per min under a N₂ atmosphere, which is maintained at a temperature of 800 °C, and its weight loss has been recorded. The measurement of N₂ adsorption–desorption isotherms was performed on a Quantachrome Autosorb iQ static N₂ physisorption device at –196 °C. Before analyzing, the sample (0.3 g) has been outgassed at 320 °C for 4 h under helium. The adsorption of functional groups and amine molecules by the zeolites has been confirmed by the FTIR spectra recorded in a Thermo Nicolet Nexus 670 spectrometer using the KBr pellet method (4000–400 cm^{–1}). The powder X-ray diffraction studies have been carried out using a diffractometer equipped with monochromatic Cu K α radiation ($k = 1.54 \text{ \AA}$). The percentage of carbon, nitrogen, hydrogen, and sulfur contents in elemental analysis has been determined using a CHNS analyzer of the Elementar Vario MICRO cube model. SEM analysis has been carried out using a Hitachi S-3000N SEM to study the

morphology of the samples. TEM analysis has been carried out on FEI of Talos make.

3. KINETICS

3.1. Adsorption Kinetics. The CO₂ adsorption kinetics data so obtained is examined by comparing it with the Lagergren pseudo-kinetic models, as shown in Table 1.

3.1.1. Pseudo-First-Order Kinetic Model. The pseudo-first-order kinetic model is used for the liquid–solid phase as shown in Table 1.²²

The values of k_1 and q_e are obtained from the slope and intercept of the plots, which are indicated in Table 1, which depicts that the rate of adsorption is directly proportional to the free active sites available on the surface of the adsorbent.

3.1.2. Pseudo-Second-Order Kinetic Model. The pseudo-second-order kinetic model is used for the liquid–solid phase as shown in Table 1, which depicts that the rate of adsorption is directly proportional to the squared number of free active sites available on the surface of the adsorbent. Many researchers preferred this model to compare the experimental data of CO₂ adsorption kinetics.^{23,24} The different slopes and intercepts have been shown in Table 1, based on the pseudo-first- and pseudo-second-order kinetic models.

The most widely and commonly used equation for a gas–solid system is assumed to follow the kinetics of first and second orders.²⁵ The models are represented by first- and second-order nonlinear eqs 1 and 2

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (1)$$

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (2)$$

where q_t and q_e are the adsorption capacities at time t and at equilibrium, respectively, and k_1 and k_2 are the mass transfer constants.¹⁹ For the boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_e$ at $t = \infty$, the integrated forms of eqs 1 and 2 become eqs 3 and 4.

$$q_t = q_e(1 - e^{(-k_1t)}) \quad (3)$$

$$q_t = q_e - \frac{q_e}{1 + ktq_e} \quad (4)$$

4. RESULTS AND DISCUSSION

4.1. Sorbent Characterization. The SEM and TEM analysis of the pristine and modified zeolites using amines have been critically performed, and their results are shown in Figure S1. The SEM images reveal the uniformity in the structures even after the amine loading, indicating no morphological change in the amine-modified zeolites and different amines such as DETA, EDA, MEA, and TEA at a constant loading percentage of 40 wt %, as shown in Figure S1a–e, respectively, which correlated with the literature.²⁴ In addition, from TEM images, it is observed that a DETA-based molecular layer is

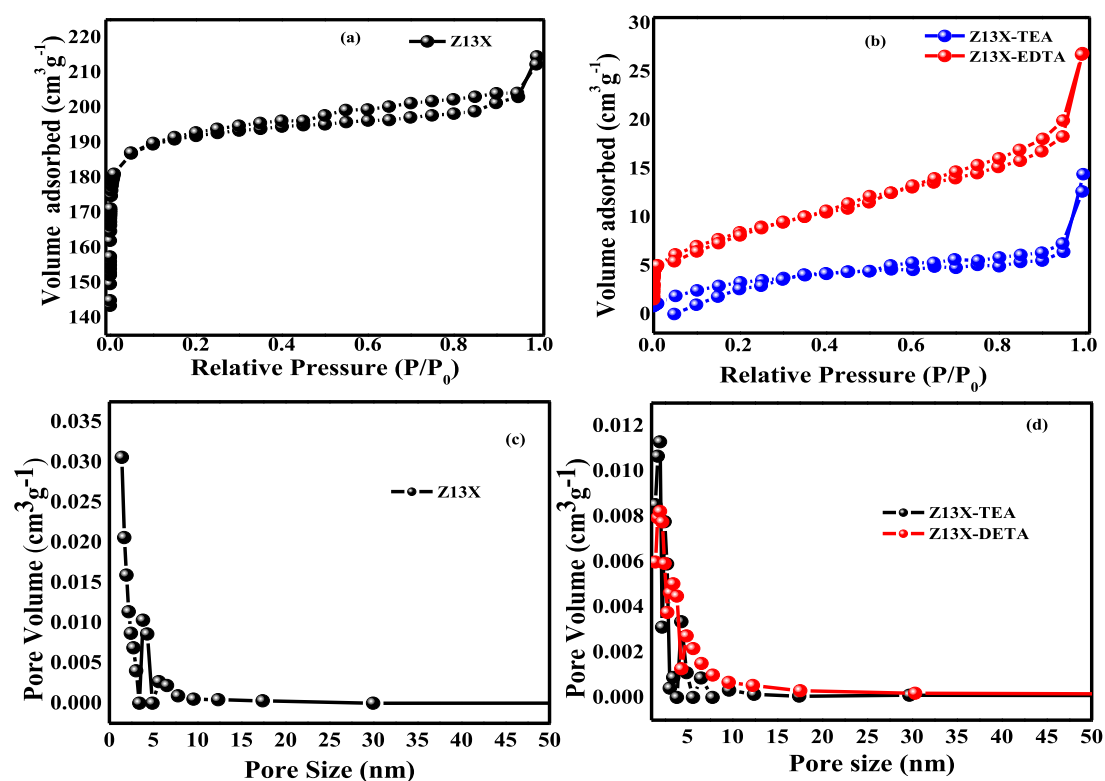


Figure 1. (a, b) N_2 adsorption–desorption isotherms of zeolites 13X, 13X-DETA-40, and 13X-TEA-40, (c, d) Barret–Joyner–Halenda (BJH) pore size distribution curves of zeolites 13X, 13X-DETA-40, and 13X-TEA-40.

laid on the solid surface of modified zeolite along with depleted crystallinity observed in the modified phase (Figure S1f,g). The results of X-ray diffraction (XRD) spectral study of different amine-based zeolites in comparison with the pristine zeolite 13X have been shown in Figure S2. After the DETA was loaded, the intensity of the diffraction peaks of zeolite 13X decreased substantially, which was probably induced by the formation of a dense layer of DETA on the surface of zeolite 13X. Fourier transform infrared spectra (Figure S3) showed that the samples have both amine and zeolite features, indicating that DETA was impregnated considerably in zeolite 13X. It can be clearly observed from the data plot that the region from 1314 to 1591 cm^{-1} has a change compared to that of zeolite 13X, indicating the N–H stretching frequency of the primary amines. The broadening of the peak has been observed in the 13X-DETA-40 composite up to 738 cm^{-1} , clearly indicating the secondary amine N–H wagging.²⁷

4.1.1. N_2 Adsorption/Desorption Isotherms. Nitrogen (N_2) adsorption–desorption isotherms of zeolite 13X, 40 wt % DETA zeolite 13X, and 40 wt % TEA zeolite 13X are shown in Figure 1a,b. The adsorption/desorption isotherm resembles the typical type-I isotherms of zeolite 13X and amine-modified zeolites, namely, 13X-DETA and 13X-TEA, respectively (according to IUPAC). The surface area of pristine zeolite 13X is 578.177 m^2/g , which tends to decrease with the amine loading to 30.751 and 35.429 m^2/g for 13X-TEA-40 and 13X-DETA-40, respectively, which envisage the doping of the amine moieties over the zeolite surfaces. The pore size distribution curve shown in Figure 1c,d depicts that 13X-DETA-40 possesses a superior pore volume of 4.082 cm^3/g , indicating the highest stability and mesoporosity.^{18,28} Classification of most microporous featuring materials which has high volume of N_2 adsorption and certain low relative

pressures.¹⁹ As this synthesis is supported by physical impregnation, it is more likely that a dense layer of DETA molecules would have covered the surface of zeolite 13X, which avoids N_2 adsorption at a low temperature of 77 K. The corresponding textural properties of the samples are listed in Table 2.

Table 2. Textural Properties of Z13X and Amine-Modified DETA and TEA at 40 wt % Loaded Samples

sample ID	S_{BET} (m^2/g)	V_{total} (cm^3/g)	D_p (nm)	V_{mean} (cm^3/g)
Z13X	578.177	0.994	2.301	3.326
13X-DETA-40	35.429	0.993	5.803	4.082
13X-TEA-40	30.751	0.995	7.813	2.150

4.1.2. Thermogravimetric Analysis. The thermal behavior of zeolite 13X and pristine zeolite 13X amine-loaded with various amounts of DETA are measured by TGA under N_2 environment and shown in Figure S4a. The samples were treated at 25–800 $^{\circ}\text{C}$ temperature at a rate of 10 $^{\circ}\text{C}/\text{min}$. As can be seen in Figure S4a, 13X zeolite presented a two-step decomposition process in the temperature range 25–400 $^{\circ}\text{C}$, and this could be attributed to the desorption of chemisorbed and physisorbed water molecules.^{19,21} Alternatively, 13X zeolite with 40, 50, and 60 wt % amines displayed multistep decomposition with a percentage weight loss of 23.05, 35.08, and 24.86, respectively, in a similar temperature range. TGA coupled with mass (TGA-MS) analysis (13X-DETA-40) clearly shows the decomposition fragments of AMU 15, 16, and 43, can be attributed to the evolved gas fragments of $-\text{NH}_3$, $-\text{NH}_2$, and $-\text{NHCH}_2\text{CH}_2$, respectively, as shown in Figure S4b–d.

4.1.3. Elemental Analysis. The elemental analysis of unmodified and modified amine DETA-13X zeolites are presented in Table 3. The result showed that amine-modified

Table 3. Elemental Analysis of Zeolite 13X and DETA Zeolite 13X

sample ID	nitrogen (wt %)	carbon (wt %)	hydrogen (wt %)
Z13X	0.00	0.00	2.51
13X-DETA-40	2.54	4.62	2.57
13X-DETA-50	6.08	10.94	3.85
13X-DETA-60	2.59	4.79	2.53

zeolites possess strong structural properties through the presented contents of nitrogen (2.54–6.08 wt %) and carbon (4.62–10.94 wt %) in zeolite 13X supported with DETA.

4.2. CO₂ Adsorption through DETA-Modified Zeolite 13X.

4.2.1. Effect of Temperature on CO₂ Adsorption Capacity.

CO₂ adsorption capacities of 40, 50, and 60 wt % DETA-impregnated zeolite 13X using 99.99% pure CO₂ gas at different temperatures of 25, 50, 75, and 100 °C have been visualized in the data represented. The maximum CO₂ adsorption capacity is observed at around 75 °C, which is found to be the optimal adsorption temperature for synthesized adsorbents. The nature of highly loaded adsorbents at temperatures up to 75 °C is mainly due to the diffusion-controlled mechanism of filling of the pores of zeolites using DETA and other amine moieties, limiting the porosity and increasing the availability of CO₂ adsorption sites on amines. The CO₂ adsorption capacities (40–60 wt %) of highly loaded adsorbents could be attributed to the declined diffusion resistance with the increase in temperatures,¹⁹ whereas at higher temperatures of around 100 °C, the CO₂ adsorption capacity is lower due to the exothermic nature of the reaction.^{19,29–31} DETA-13X at 40 wt % shows higher levels of CO₂ adsorption, which is in contradiction to other zeolites and amine moieties, indicating the stability of the composite and higher adsorption capacity of the 13X-DETA composite at 40 wt % (Z13X, Z4A, Z5A, TEA-13X, etc.).^{32,33} The data has been tabulated in Tables 4 and S1 which is pictographically represented in Figure 2a–c. Figure S5a shows the CO₂ adsorption capacity of zeolites measured for pure CO₂ at 1 atm and 75 °C. Table S2, Figures S5b and S6–S9 depict the CO₂ adsorption capacity of the modified zeolites at different temperatures. The CO₂ adsorption capacity studies with various amine loading percentages reveal that a gradual increase in the loading percentages of amines over the zeolite surface tends to show a higher adsorption capacity at an optimal 40 wt % loading. The gradual decreases in most of the amines at 50 and 60 wt % are in agreement with the literature reported so far that the amine-modified zeolites tend to show higher adsorption capacities at optimal conditions as seen in Table S3.²⁷

4.2.2. CO₂ Adsorption Capacity in Lab-Scale Reactor.

From the various studies carried out on the microscale level, it has been observed that 13X-DETA-40 tends to possess higher adsorption capacity in comparison with the other synthesized materials, and a comparison with zeolite 13X has been shown in Figure 2a. In a lab-scale reactor, 13X-DETA-40 tends to possess superior adsorption capacity of about 1.690 mmol/g of CO₂. The CO₂ adsorption capacity with the time profile is included in the Supporting Information, as shown Figure S10,

Table 4. Scale-Up of Adsorption Capacities of Zeolite 13X over the Different Amine-Modified Adsorbents Using Pure CO₂ at 1 atm and 75 °C

sample ID	q_{exp} (mmol/g)	adsorption capacity of amine zeolites/adsorption capacity of 13X
13X	0.417	1.00
13X-DETA-40	1.054	2.53
13X-EDA-40	0.156	0.37
13X-MEA-40	0.374	0.89
13X-TEA-40	0.111	0.26
Z4A	0.600	1.43
Z4A-DETA-40	0.135	0.32
Z4A-EDA-40	0.274	0.65
Z4A-MEA-40	0.238	0.57
Z4A-TEA-40	0.370	0.88
Z5A	0.196	0.47
Z5A-DETA-40	0.138	0.33
Z5A-EDA-40	0.166	0.39
Z5A-MEA-40	0.043	0.10
Z5A-TEA-40	0.243	0.58

which confirms the higher adsorption capacity of 13X-DETA-40 in comparison with that of the pristine zeolite 13X.

4.2.3. Effect of DETA Loading on CO₂ Adsorption Capacity. Zeolite 13X modified with DETA was prepared to check its effect on CO₂ adsorption capacity. Here, we showed that the CO₂ adsorption capacities decreased as the amine loadings increased from 40 to 60 wt %, and the sorbent with 40 wt % DETA showed the maximum uptake of CO₂.²⁷ The CO₂ adsorption capacities of the present study in comparison with the literature reports have been tabulated in Table 5.

4.2.4. Kinetic Modeling. Theoretically, CO₂ adsorption on DETA-, EDA-, MEA-, and TEA-grafted zeolites 13X, 4A, and 5A could be reported in two reaction models mentioned earlier. Figure 3a,b shows the DETA-impregnated zeolite 13X at 75 °C and with 40 wt % amine loading with CO₂ uptake along with the curves produced by fitting models. The squared correlation coefficient (R^2) for regressions, along with kinetic parameters, is given in Table 6. From the results, it is concluded that the kinetic model of the pseudo-first and pseudo-second order shows the best fit, which describes the behavior of CO₂ adsorption on DETA-40-grafted 13X zeolite at an optimum temperature.

The Arrhenius equation (eq 5) describes the temperature dependence of the kinetic constants k_1 and k_2 .

$$k = A e^{-E_a/RT} \quad (5)$$

where A is the Arrhenius pre-exponential factor, E_a is the activation energy, R is the universal ideal gas constant, and T is the absolute temperature. The plot of $\ln(k)$ vs $1/T$ is given in Figure 4a,b, and the activation energy (E_a) value is specified in Table 7. A comparison of the activation energy among the pristine and amine-modified zeolites is shown in Table S4.

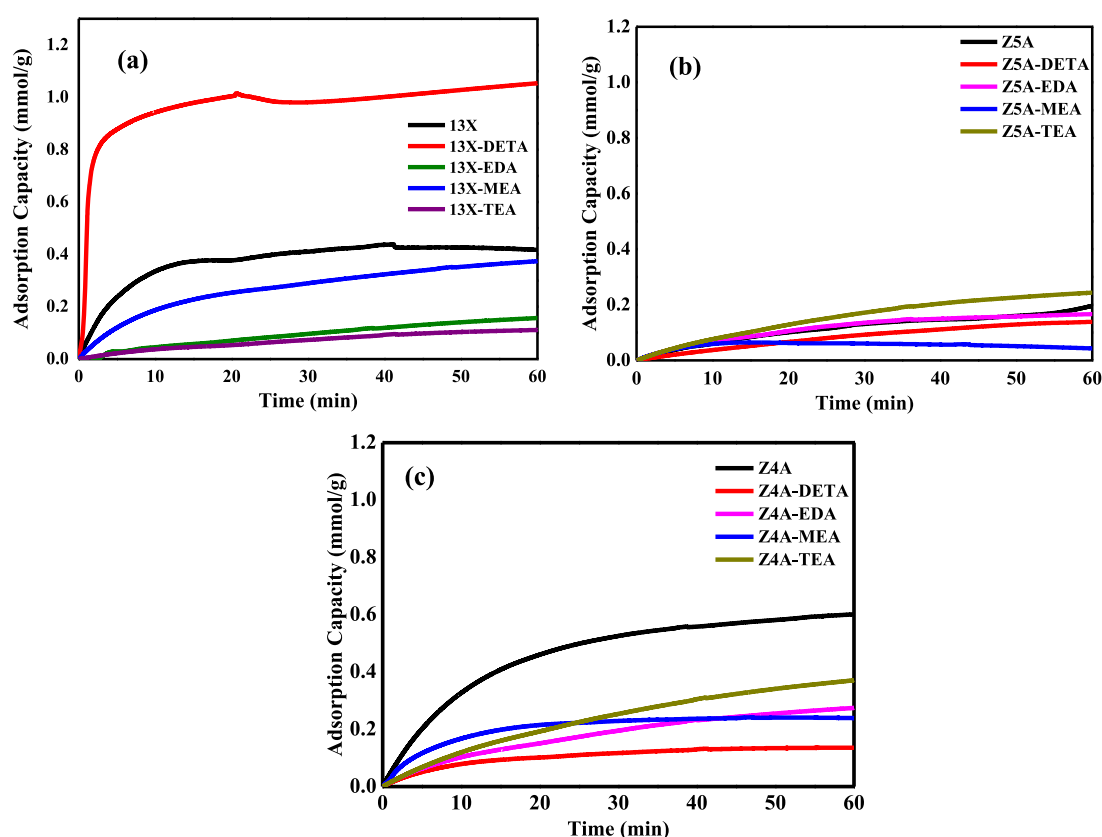


Figure 2. (a) Adsorption capacity of unmodified Z13X and modified 40 wt % Z13X-DETA, EDA, MEA, and TEA. (b) CO₂ adsorption capacity of 40 wt % DETA, EDA, MEA, and TEA on zeolite Z5A. (c) CO₂ adsorption capacity of 40 wt % DETA, EDA, MEA, and TEA on zeolite Z4A measured for pure CO₂ at 1 atm and 75 °C.

Table 5. Comparison of Adsorption Capacities for DETA-Loaded Adsorbents

adsorbent	amine loading (wt %)	CO ₂ adsorption capacity (mmol/g)	temp (°C)	pressure (atm)	refs
13X-DETA (microscale)	40	1.054	75	1	this study
13X-DETA (lab-scale reactor)	40	1.690	75	1	this study
13X-PEI600000MWa	60	1.220	75	1	19
Meso-13X-PEI800MW	33	1.320	75	1	21
13X		0.360	75	1	26
13X-MEA	50	0.450	75	1	26
TETA-ZSM-5	30	1.200	50		31
Z4A-IBA	0.3	2.560	25	1	32
NaY-TEPA	10	2.100	75	1	34
Y60-TEPA	50	3.300	60		35

4.3. Process Optimization. Detailed process optimization studies were conducted for this experiment keeping in view the cost of experimentation. Detailed process flow charts are shown in Figures 6 and 7 for microscale and lab-scale reactor experimentation, respectively. It is imperative to mention here that the process optimization studies for reactor-scale experimentation are still under development and an investigative report for the same would be released in the near future.

4.3.1. Microscale Experimentation. On the microscale level, as mentioned earlier in the Results and Discussion Section, an array of zeolites were selected and impregnated with amines to identify the adsorption capacities of the amines. Cost analysis was conducted for these zeolites to ascertain the optimum candidates for lab-reactor-scale experimentation. For this, the zeolites not only must satisfy the adsorption capacity minima but also are required to show low investment per ton of CO₂. Results of cost analysis are tabulated below in Table 8. Detailed computational procedures for the cost analysis at the microscale level were performed and shown in Table S5a–c. From the results of the microscale experimentation, two zeolites, 13X and 13X-DETA-40, were identified as likely candidates for lab-scale reactor experimentation due to their relatively low investment per ton of CO₂ adsorbed. Zeolite 13X-DETA-40 especially warranted special attention due to its relatively high adsorption capacity as well.

4.3.2. Lab-Scale Reactor. Zeolites 13X and 13X-DETA-40 were subjected to cost analysis for experimentation in a lab-scale reactor fabricated for adsorption studies. The results of the experimentation are listed in Table 9. Detailed information regarding computational costs is included in Table S6a–d.

The cost analysis study carried out so far revealed that the cost has been significantly reduced from the microscale to the lab-scale reactor. Zeolite 13X-DETA-40 especially showed a reduction of 84% in investment from \$49,830/ton CO₂ adsorbed to \$7,690/ton CO₂ adsorbed.

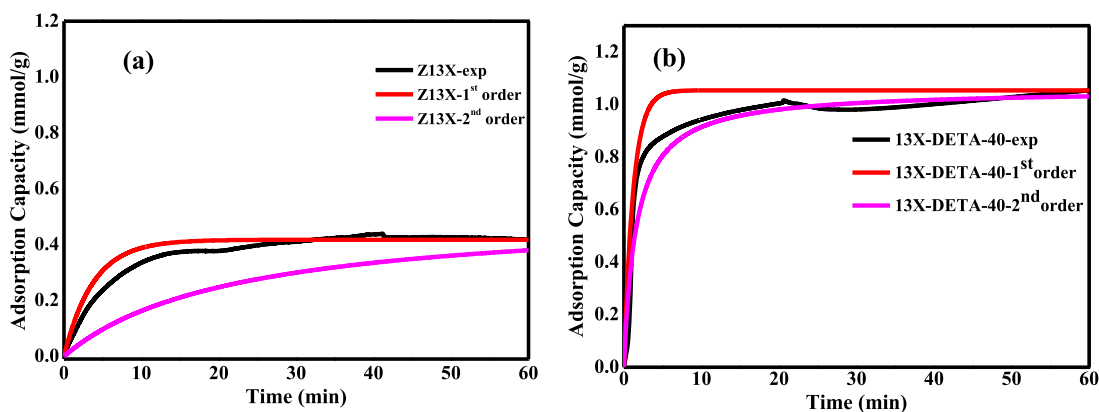


Figure 3. (a, b) Adsorption studies with the first- and second-order kinetic models of the unmodified and the amine-loaded zeolite 13X with 40 wt % DETA precisely measured at 1 atm and 75 °C.

Table 6. Pseudo-First- and Pseudo-Second-Order Kinetic Parameters of Unmodified and Modified 40 wt % DETA, EDA, MEA, and TEA on 13X, 4A, and 5A Zeolites Measured for Pure CO₂ at 1 atm and 75 °C

sample ID	kinetic parameters						
	experimental		first order			second order	
	q_{exp} (mmol/g)	q_e (mmol/g)	k_1 (min ⁻¹)	R^2	q_e (mmol/g)	k_2 (min ⁻¹)	R^2
13X	0.417	0.418	0.265	0.968	0.379	0.089	0.986
13X-DETA-40	1.054	1.055	0.842	0.990	1.058	0.602	0.998
13X-EDA-40	0.156	0.157	0.016	0.990	0.224	0.137	0.977
13X-MEA-40	0.374	0.376	0.128	0.878	0.454	0.145	0.993
13X-TEA-40	0.111	0.114	0.018	0.995	0.187	0.125	0.989
Z4A	0.600	0.610	0.243	0.957	0.729	0.112	0.998
Z4A-DETA-40	0.135	0.136	0.057	0.987	0.163	0.543	0.997
Z4A-EDA-40	0.274	0.027	0.059	0.960	0.402	0.083	0.982
Z4A-MEA-40	0.238	0.239	0.135	0.992	0.269	0.637	0.994
Z4A-TEA-40	0.370	0.371	0.062	0.943	0.631	0.037	0.998
Z5A	0.196	0.275	0.109	0.993	0.197	0.036	0.990
Z5A-DETA-40	0.138	0.139	0.016	0.998	0.310	0.045	0.999
Z5A-EDA-40	0.166	0.166	0.047	0.997	0.231	0.192	0.996
Z5A-MEA-40	0.043	0.044	0.051	0.955	0.048	0.130	0.981
Z5A-TEA-40	0.243	0.244	0.404	0.991	0.433	0.051	0.990

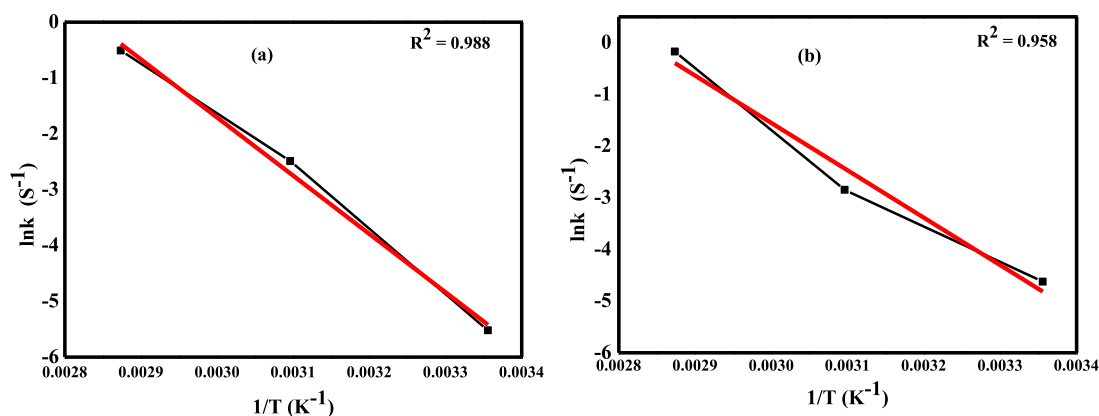


Figure 4. (a) Arrhenius plots for the kinetic constants obtained by first- and (b) second-order kinetic models of 13X-DETA-40.

Table 7. Pseudo-First- and Pseudo-Second-Order Values of Activation Energy for 13X-DETA-40

model	E_a (kJ/mol)
Pseudo-first order	86
Pseudo-second order	76

5. CONCLUSIONS

The zeolite-based adsorbents were prepared and tested for the CO₂ capture study from simulated gas mixtures by TGA (microscale) analysis and a lab-scale reactor column. Four different types of amines were impregnated on various zeolites to investigate the amine zeolite composites' performance for

Table 8. Cost Efficiency of Zeolite and Amine Zeolites

sample ID	mmol CO ₂ adsorbed/g of zeolite	investment/ton of CO ₂ adsorbed (x\$1,000/ton)
Z4A	0.600	16.56
Z5A	0.196	17.19
13X	0.417	22.17
13X-DETA-40	1.054	49.83
13X-MEA-40	0.374	139.02
Z4A-TEA-40	0.370	167.45
Z4A-EDA-40	0.274	230.02
Z5A-TEA-40	0.243	253.47
Z4A-MEA-40	0.238	265.21
13X-EDA-40	0.156	332.75
Z5A-EDA-40	0.166	377.72
13X-TEA-40	0.111	459.33
Z5A-DETA-40	0.138	459.70
Z4A-DETA-40	0.135	472.11
Z5A-MEA-40	0.043	1460.49

CO₂ adsorption. The texture and surface chemistry of the thus-prepared material were investigated through CO₂ adsorption studies, SEM, TEM, XRD, TGA, FTIR, and CHNS analyses. Further, an effort was made to characterize the properties of the developed adsorbents. The results depicted that the CO₂ adsorption capacity increased to optimal values (40 wt % DETA) and further declined on increasing the amine loading percentage. For MEA-, EDA-, and TEA-loaded adsorbents, the CO₂ uptake capacity decreased with an increase in the adsorption temperature. In the DETA-loaded adsorbent, the maximum adsorption capacity was observed at 75 °C, and the capture capacity of the 40-DETA-13X sorbent was 1.054 mmol/g (TGA, microscale) and that in the lab-scale reactor was 1.69 mmol/g CO₂. Adsorption kinetics data on the adsorbents were described using the pseudo-first- and pseudo-second-order kinetic models. It was observed that the kinetic models were well corroborated with the CO₂ adsorption kinetics data. Activation energy on the DETA-modified zeolites increased, followed by a decrease above the optimal conditions. A further refinement of the process could result in a novel method of CO₂ adsorption that could be adopted at an industrial scale.

6. EXPERIMENTAL SECTION

6.1. Materials. The different classes of amines used in the present study were of analytical grade. DETA, EDA, MEA, and

TEA solutions and zeolite 13X powder (2 μm), 4A, and 5A were obtained from Sigma-Aldrich, USA, and utilized without any further distillation as well as purification. Methanol was acquired from Finar Limited, India. The CO₂ and nitrogen cylinders were procured from Vijay Enterprises, Secunderabad and Telangana, India.

6.2. Synthesis of Amine-Modified Zeolite Adsorbent.

The loadings of DETA, EDA, MEA, and TEA were anchored on commercial zeolites 13X, 4A, and 5A through a physical impregnation method as carried out by Xu et al.³⁶ The schematic representation of the adsorbent preparation method is depicted in Figure 5a, and the flow chart for the same can be seen in Figure 5b. The structures of amines are tabulated in Table 10.³⁷

The immobilizations of amines (DETA, EDA, MEA, and TEA) over zeolites were performed through the alcoholic solutions of amines. A desired amount of amine was dissolved in distilled methanol and stirred for 15 min. Zeolite (13X, 4A, and 5A; 2 g) was suspended into the prepared solution. Then, the obtained slurry was continuously stirred for 4 h and the solid–liquid ratio was maintained as 1:2 throughout the preparation of adsorbents. Furthermore, the resulting mixture was filtered and dried in an oven at 70 °C overnight. The prepared adsorbents were denoted 13X-(DETA, EDA, MEA, and TEA)-*n*, 4A-(DETA, EDA, MEA, and TEA)-*n*, and 5A-(DETA, EDA, MEA, and TEA)-*n*, where *n* represents the loading of DETA, EDA, MEA, and TEA as the wt % in the sample.

6.3. CO₂ Adsorption Studies. 6.3.1. Microscale Study.

TGA (SDT Q600, TA Instruments) was used for CO₂ adsorption studies, which provides an outcome in the form of CO₂ uptake (in mg), which was maintained under desired conditions with respect to time.^{19,38,39} The measurements of CO₂ adsorption capacity were performed with 99.99% pure CO₂, and nitrogen was used as an inert gas in the pretreatment process. Zeolite samples were appropriately ground to form uniform size particles, and 20 mg of the sample is put into an alumina pan. The loading samples were initially subjected to pretreatment at 100 °C in the presence of nitrogen gas at a flow rate of 50 mL per min before starting the experiment. Later, the sample was held up to 60 min, and the instrument was cooled down to the desired temperatures, which were 25, 50, 75, and 100 °C. As the temperature was equilibrated up to desired levels, the gas was adjusted from pure N₂ to pure CO₂ at a flow rate of 50 mL per min. The process flowsheet for the experiment is included below in Figure 6. Equation 6 was used to determine the amount of CO₂ molecules adsorbed onto the synthesized modified zeolites (mg/g). *W*₀ and *W*_{*t*} denoted the original mass of the adsorbent and the mass of the adsorbent at time *t*.

$$\text{CO}_2 \text{ adsorption} = \frac{W_t(\text{mg}) - W_0(\text{mg})}{W_0(\text{g})} \quad (6)$$

Table 9. Absorption Capacity and Investment per Ton of CO₂ Adsorbed for Zeolites 13X and 13X-DETA-40

sample ID	adsorption capacity (mmol CO ₂ /g zeolite) (microscale)	adsorption capacity (mmol CO ₂ /g zeolite) (lab-scale reactor)	investment/ton of CO ₂ adsorbed (x\$1,000/ton) (microscale)	investment/ton of CO ₂ adsorbed (x\$1,000/ton) (lab-scale reactor)
13X	0.417	0.717	22.17	3.27
13X-DETA-40	1.054	1.690	49.83	7.69

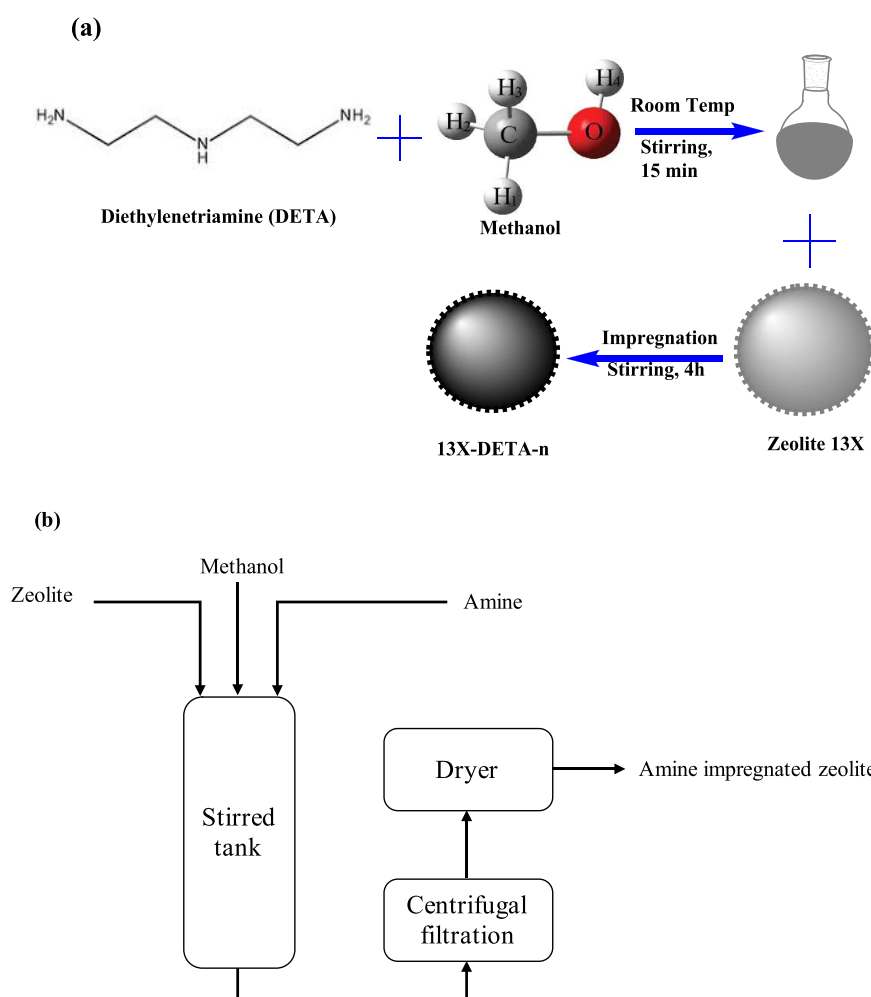


Figure 5. (a) Schematic diagram of adsorbent preparation; (b) process flow chart for amine impregnation of zeolites.

Table 10. Structures of Amines Used for Adsorbent Functionalization

Name of Amines	Structure
Diethylenetriamine (DETA)	
Ethylenediamine (EDA)	
Monoethanolamine (MEA)	
Triethanolamine (TEA)	

6.3.2. Lab-Reactor Scale. In the lab-reactor-scale experimentation, zeolites identified through cost analysis are subjected to experimentation. In the second phase of experimentation (lab-scale reactor), upon review of results obtained from phase 1 (microscale), selected amines were used in a reactor that was fabricated for the experiments. The selected zeolite (5 g) was loaded into the packed column at 75 °C temperature, and N₂ gas was used as a carrier gas.

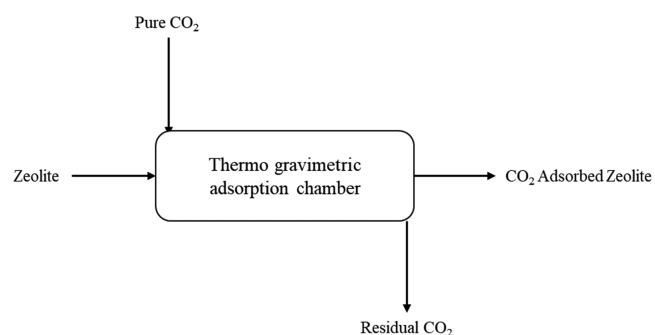


Figure 6. Process flow chart of microscale experimentation.

Simultaneously, CO₂ gas was passed through it at 1 atmospheric pressure for analysis. At the exit, the final product was collected and injected into the GC-TCD instrument with the injector temperature of 100 °C, column temperature of 120 °C, and TCD temperature of 200 °C with a nitrogen flow rate of 30 mL per min. The same procedure was carried out for the lab-scale reactor setup, and the setup flow chart has been shown in Figure 7.

7. FUTURE LINE OF WORK

The foremost objective would be to study the impact of surface area on the zeolite adsorption capacity, focusing on 13X-DETA-40. A design of experiments would be developed and

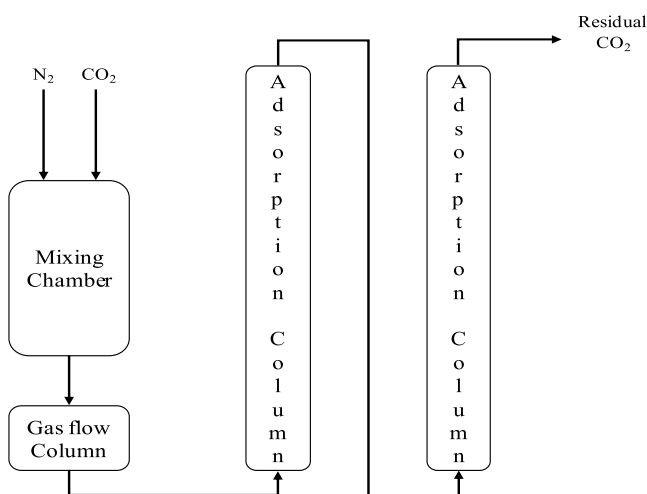


Figure 7. Process flow chart of lab-scale reactor experimentation.

used for studying the adsorption of various zeolite and amine combinations in a microscale system. A further refinement of the process would also be conducted to reduce the costs and form a basis for the investment for adsorption capacity studies.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.0c05397>.

SEM and TEM images of 13X zeolite and amine-modified 13X zeolites; XRD studies and XRD spectra; FTIR studies and FTIR spectra; profile of TGA; CO₂ adsorption kinetics of the zeolites; and the modified amine-loaded zeolites with cost analysis (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Siriwardane, R. V.; Shen, M. S.; Fisher, E. P. Adsorption of CO₂, N₂, and O₂ on Natural Zeolites. *Energy Fuels* **2003**, *17*, 571–576.
- (2) White, C. M.; Strazisar, B. R.; et al. Separation and Capture of CO₂ from Large Stationary Sources and Sequestration in Geological Formations—Coalbeds and Deep Saline Aquifers. *J. Air Waste Manage. Assoc.* **2003**, *53*, 645–715.
- (3) Aaron, D.; Tsouris, C. Separation of CO₂ from Flue Gas: A Review. *Sep. Sci. Technol.* **2005**, *40*, 321–348.
- (4) Wang, J.; Long, D.; Zhou, H.; Chen, Q.; Liu, X.; Ling, L. Surfactant promoted solid amine sorbents for CO₂ capture. *Energy Environ. Sci.* **2012**, *5*, 5742–5749.
- (5) Leung, D. Y. C.; Caramanna, Valer, M. M. An Overview of Current Status of Carbon Dioxide Capture and Storage Technologies. *Renewable Sustainable Energy Rev.* **2014**, *39*, 426–443.
- (6) Hwang, C. C.; Tour, J. J.; Kittrell, C.; Espinal, L.; Alemany, L. B.; Tour, J. M. Capturing Carbon Dioxide as a Polymer from Natural Gas. *Nat. Commun.* **2014**, *5*, No. 3961.
- (7) Kapdi, S. S.; Vijay, V. K.; Rajesh, S. K.; Prasad, R. Biogas Scrubbing, Compression and Storage: Perspective and Prospectus in Indian Context. *Renewable Energy* **2005**, *30*, 1195–1202.
- (8) Pardakhti, M.; Jafari, T.; Tobin, Z.; Dutta, B.; Moharreri, E.; Shemshaki, N. S.; Suib, S.; Srivastava, R. Trends in Solid Adsorbent Materials Development for CO₂ Capture. *ACS Appl. Mater. Interfaces* **2019**, *11*, 34533–34559.
- (9) Hu, X. E.; Liu, L.; Luo, X.; Xiao, G.; Shiko, E.; Zhang, R.; Fan, X.; Zhou, Y.; Liu, Y.; Zeng, Z.; Li, C. E. A review of N-functionalized solid adsorbents for post-combustion CO₂ capture. *Appl. Energy* **2020**, *260*, No. 114244.
- (10) Hu, X. E.; Qian, Y.; Francesco, B.; Chao'en, L.; Maohong, F.; Gasem, K. A. M.; Zhang, X.; Shiko, E.; Mi, T.; Xiao, L.; Zeng, Z.; Liu, Y.; Zhang, R. NMR Techniques and Prediction Models for the Analysis of Species Formed in CO₂ Capture Processes with Amine-Based Sorbents: A Critical Review. *ACS Sustainable Chem. Eng.* **2020**, *8*, 6173–6193.
- (11) Akhtar, F.; Andersson, L.; Keshavarzi, N.; Bergstrom, L. Colloidal Processing and CO₂ Capture Performance of Sacrificially Templated Zeolite Monoliths. *Appl. Energy* **2012**, *97*, 289–296.
- (12) Xu, X.; Song, C.; Andersen, J. M.; Miller, B. G.; Scaroni, A. W. Novel Polyethylenimine-Modified Mesoporous Molecular Sieve of MCM-41 Type as High-Capacity Adsorbent for CO₂ Capture. *Energy Fuels* **2002**, *16*, 1463–1469.
- (13) Lv, X.; Li, L.; Tang, Wang, C.; Zhao, X. High CO₂/N₂ and CO₂/CH₄ Selectivity in a Chiral Metal-Organic Framework with Contracted Pores and Multiple Functionalities. *Chem. Commun.* **2014**, *50*, 6886–6889.
- (14) Plaza, M. G.; Pevida, A. S. G. C.; Rubiera, F.; et al. Valorisation of Spent Coffee Grounds as CO₂ Adsorbents for Postcombustion Capture Applications. *Appl. Energy* **2012**, *99*, 272–279.

- (15) Plaza, M. G.; Gonzalez, A. S.; Pis, J. J.; Rubiera, F.; et al. Production of Microporous Biochars by Single-Step Oxidation; Effect of Activation Conditions on CO₂ Capture. *Appl. Energy* **2014**, *114*, 551–562.
- (16) Broda, M.; Muller, C. R. Sol-Gel-Derived, CaO-Based, ZrO₂-Stabilized CO₂ Sorbents. *Fuel* **2014**, *127*, 94–100.
- (17) Valverde, J. M.; Jimenez, P. E. S.; Perejon, A.; Maqueda, L. A. P. Constant Rate Thermal Analysis for Enhancing the Long-Term CO₂ Capture of CaO at Ca-Looping Conditions. *Appl. Energy* **2013**, *108*, 108–120.
- (18) Bezerra, D. P.; da Silva, W. M.; de Moura, P. A. S.; Sousa, A. G. S.; Vieira, R. S.; Castellon, E. R.; Azevedo, D. C. S. CO₂ adsorption in amine-grafted zeolite 13X. *Appl. Surf. Sci.* **2014**, *314*, 314–321.
- (19) Karka, S.; Kodukula, S.; Nandury, S. V.; Pal, U. Polyethylenimine-Modified Zeolite 13X for CO₂ Capture: Adsorption and Kinetic Studies. *ACS Omega* **2019**, *4*, 16441–16449.
- (20) Jadhav, P. D.; Chatti, R. V.; Biniwale, R. B.; Labhsetwar, Nitin.; Devotta; Rayalu, S. Monoethanol Amine Modified Zeolite 13X for CO₂ Adsorption at Different Temperatures. *Energy Fuels* **2007**, *21*, 3555–3559.
- (21) Chen, C.; Kim, S. S.; Seung, C. W.; Ahn, W. S. Polyethylenimine Incorporated Zeolite 13X with Mesoporosity for Post-Combustion CO₂ Capture. *Appl. Surf. Sci.* **2015**, *332*, 167–171.
- (22) Singh, V. K.; Kumar, E. A. Comparative Studies on CO₂ Adsorption Kinetics by Solid Adsorbents. *Energy Procedia* **2016**, *90*, 316–325.
- (23) Ho, Y. S. Second-order kinetic model for the sorption of cadmium onto tree fern; A comparison of linear and non-linear methods. *Water Res.* **2006**, *40*, 119–125.
- (24) Zhang, Z.; Huang, S.; Xian, S.; Xi, H.; Li, Z. Adsorption Equilibrium and Kinetics of CO₂ on Chromium Terephthalate MIL101. *Energy Fuels* **2011**, *25*, 835–842.
- (25) Simonin, J. P. On the comparison of pseudo-first order and pseudo-second order rate laws in the modeling of adsorption kinetics. *Chem. Eng. J.* **2016**, *300*, 254–263.
- (26) Chatti, R.; Bansawal, A.; Thote, J. A.; Kumar, V.; Jadhav, P.; Lokhande, S. K.; Biniwale, R.; Labhsetwar, N.; Rayalu, S. Amine Loaded Zeolite for Carbon Dioxide Capture; Amine Loading and Adsorption Studies. *Microporous Mesoporous Mater.* **2009**, *121*, 84–89.
- (27) Liu, L.; Chen, H.; Shiko, E.; Fan, X.; Zhou, Y.; Zhang, G.; Luo, X.; Hu, X. E. Low-cost DETA impregnation of acid-activated sepiolite for CO₂ capture. *Chem. Eng. J.* **2018**, *353*, 940–948.
- (28) Siriwardane, R. V.; Shen, M. S.; Fisher, E. P.; Losch, J. Adsorption of CO₂ on Molecular Sieves and Activated Carbon. *Energy Fuels* **2001**, *15*, 279–284.
- (29) Lin, Z.; Wei, J.; Geng, L.; Mei, D.; Liao, L. Adsorption of carbon dioxide by a novel amine impregnated ZSM-5/KIT-6 composite. *RSC Adv.* **2017**, *7*, 54422–54430.
- (30) Wei, M.; Yu, Q.; Duan, W.; Hou, L.; Qin, Q.; Liu, S.; Dai, J.; et al. Equilibrium and Kinetics Analysis of CO₂ Adsorption on Waste Ion-Exchange Resin-Based Activated Carbon. *J. Taiwan Inst. Chem. Eng.* **2017**, *77*, 161–167.
- (31) Dinda, S.; Murge, P.; Paruchuri, B. C. A study on zeolite-based adsorbents for CO₂ capture. *Bull. Mater. Sci.* **2019**, *42*, No. 240.
- (32) Panda, D.; Kumar, E. A.; Singh, S. K. Amine Modification of Binder-Containing Zeolite 4A Bodies for Post-Combustion CO₂ Capture. *Ind. Eng. Chem. Res.* **2019**, *58*, 5301–5313.
- (33) Siriwardane, R. V.; Shen, M. S.; Fisher, E. P.; Losch, J. Adsorption of CO₂ on Zeolites at Moderate Temperatures. *Energy Fuels* **2005**, *19*, 1153–1159.
- (34) Babaei, M.; Anbia, M.; Kazemipour, M. Enhancement of CO₂/CH₄ Adsorptive Selectivity by Functionalized Nano Zeolite. *J. Ultrafine Grained Nanostruct. Mater.* **2018**, *51*, 174–182.
- (35) Su, F.; Lu, C.; Kuo, S. C.; Zeng, W. Adsorption of CO₂ on Amine-Functionalized Y-Type Zeolites. *Energy Fuels* **2010**, *24*, 1441–1448.
- (36) Xu, X.; Song, C.; Andersen, J. M.; Miller, B. G.; Scaroni, A. W. Preparation and Characterization of Novel CO₂ “Molecular Basket” Adsorbents Based on Polymer-Modified Mesoporous Molecular Sieve MCM-41. *Microporous Mesoporous Mater.* **2003**, *62*, 29–45.
- (37) Samanta, A.; Zhao, A.; Shimizu, G. K. H.; Sarkar, P.; Gupta, R. Post-combustion CO₂ capture using solid sorbents: A Review. *Ind. Eng. Chem. Res.* **2012**, *51*, 1438–1463.
- (38) Rashidi, A. N.; Yusup, S.; Loong, L. H. Kinetic Studies on Carbon Dioxide Capture Using Activated Carbon. *Chem. Eng. Trans.* **2013**, *35*, 361–366.
- (39) Liu, Z.; Pudasainee, D.; Liu, Q.; Gupta, R. Post-Combustion CO₂ Capture Using Polyethylenimine Impregnated Mesoporous Cellular Foams. *Sep. Purif. Technol.* **2015**, *156*, 259–268.