

Removal of CO₂ in a Multi Stage Fluidized Bed Reactor by Monoethanolamine Functionalize Activated Carbon

Dipa Das¹ and B. C. Meikap^{1, 2*}

¹Department of Chemical Engineering, Indian Institute of Technology (IIT) Kharagpur, West Bengal, India.

²Department of Chemical Engineering, School of Engineering, Howard College, University of Kwazulu-Natal (UKZN), King George V Avenue, Durban 4000, South Africa.

Abstract: In the present a multi-stage stage fluidized bed reactor has been developed and designed for removal of CO₂. The adsorbents used for this fluidized bed reactor were monoethanolamine functionalize activated carbon (MEA-AC) and activated carbon (AC) The maximum % removal of CO₂ for MEA-AC (0.6) was 94.9%.

Keywords: Monoethanolamine, Activated carbon, Adsorbent, Carbon dioxide, Multistage fluidized bed

1. Introduction

The concentration of CO₂ causes global warming and climate change [1]. For removal of CO₂ from flue gas, adsorption process is a very simple and cost-effective [2]. The activated carbon (AC) surface chemistry is also an important criteria [3-4] during adsorption process. CO₂ is coming under acidic pollutants. It is one of the most prominent methods for attachment of amine functional group on their surfaces [5-6]. Amine-modified solid sorbents have high CO₂ adsorption capacity and moisture tolerance [7-8] and suitable for CO₂ capture.

For recovery of gaseous pollutants that coming out from industry, multistage fluidized bed reactor with a down comer has recently gained importance [8-11]. In our present investigation, a multistage fluidized bed reactor designed for adsorption of CO₂ gas on monoethanol amine functionalize activated carbon by fluidized bed adsorption process.

2. Materials and Methods

2.1.Preparation of Sorbent

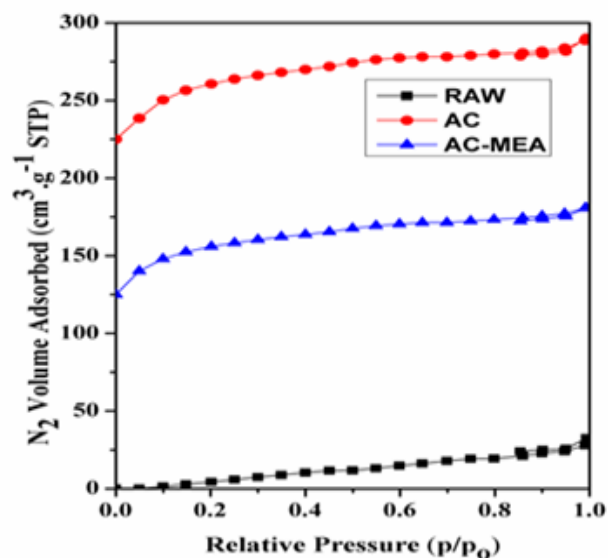
The raw material used for preparation of amine impregnated activated carbon was green coconut shells. After washing and cutting to smaller size, it was kept in the sunlight for 20-30 days till it becomes completely dry. Dried green coconut shells were put inside the hot air oven at 105 °C for 36 h for removal of moisture and other volatile matter. The dried samples were crushed with a locally made crusher and sieved to a size of 512 µm. Chemical activation was done with ZnCl₂ in the impregnation ratio (1:1). The dried AC was impregnated with monoethanolamine solution (OH-CH₂-CH₂-NH₂) of different impregnation ratio. Amine-impregnated AC was dried in the hot air oven at temperature 105 °C for 24 h till it becomes dry and kept inside an air tight container for the experimental purpose.

2.2 Adsorbent Characterization

Table 1 shows the data related to total surface area, micropore volume and micropore surface area for amine impregnated activated carbon particle, activated carbon particle and raw precursor. Fig.1 shows the N₂ adsorption isotherms and it is of Type I, which represents dense micropore structures [12].

TABLE 1: Pore Structure Parameter of MEA-AC (0.4)

Samples	S_{BET} (m^2/g)	V_T (cm^3/g)	M.P.V (cm^3/g)	Avg. Pore Radius (\AA)	Micro Pore Area (m^2/g)
Raw	59.73	0.050	0	16.84	0
AC	995.79	0.442	0.372	9.01	921.51
MEA-AC (0.4)	569.35	0.279	0.201	9.81	488.71

Fig.1: N₂ adsorption isotherm

3. Experimental Set up and Procedure

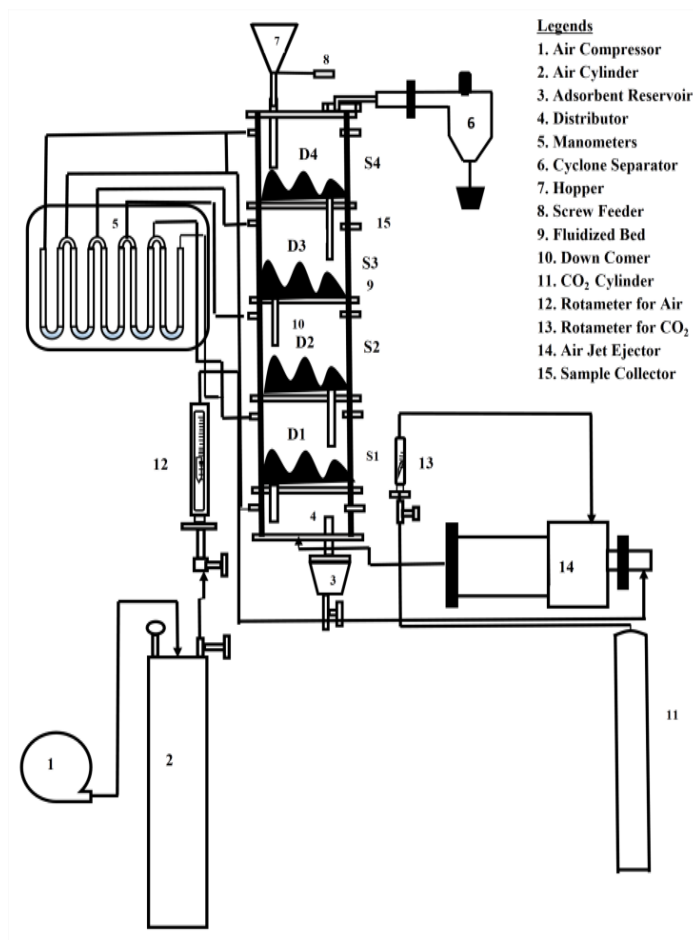


Fig. 2: Experimental set-up for four stage fluidized bed reactor

The schematic diagram of four-staged fluidized bed reactor has been shown in Fig. 2. The fluidized bed column was consisted of four stages (0.21m height per stage and 0.09 m internal diameter). Stages were assembled together with a flanged joint. Four number of stainless steel made plate (S1, S2, S3, and S4) of 0.002 m thick were used as internal baffles between two stages. Hole of diameter 0.002 m on a triangular pitch arrangement was there on each plate.

The solids were fed from the top through the screw feeder to the first stage of the down comer of the reactor. Compressed air at 2 kg/cm² pressure and (80-150) L/min flow rate was passed through the pipe line and regulated by valve. At that time CO₂ from the cylinder was passed through a gas regulator at certain flow rate. CO₂ and air mixture was passed through the throat of the ejector and the mixture was fed into the gas chamber at the bottom stage of the fluidized bed reactor. The concentration of CO₂ in CO₂ + air mixture were analyzed by the “Orsat Analysis” method. MEA-AC with different impregnation ratio samples are used for this experiment as an adsorbent.

3.1.Sampling and Analysis

The Orsat apparatus was used for analysis of CO₂ and is shown in Fig.3. The % removal of CO₂ has been calculated for each experimental run by equation (1).

$$\% \text{ Removal of CO}_2 = \frac{\text{CO}_2 \text{ inlet} - \text{CO}_2 \text{ outlet}}{\text{CO}_2 \text{ inlet}} \times 100 \quad (1)$$

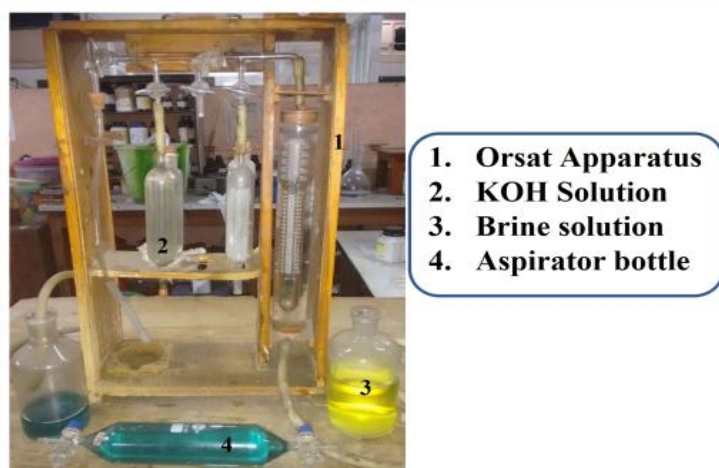


Fig. 3: Orsat apparatus

4. Results and Discussion

4.1. Effect of Impregnation Ratio on % Removal of CO₂ and Comparison with AC

Fig.4 shows the effect of different MEA impregnated AC and AC on % CO₂ removal. It has been seen from the figure that the % removal of CO₂ for MEA-AC (0.6) was highest. The MEA has functional group of –NH₂ and it is a primary amine.

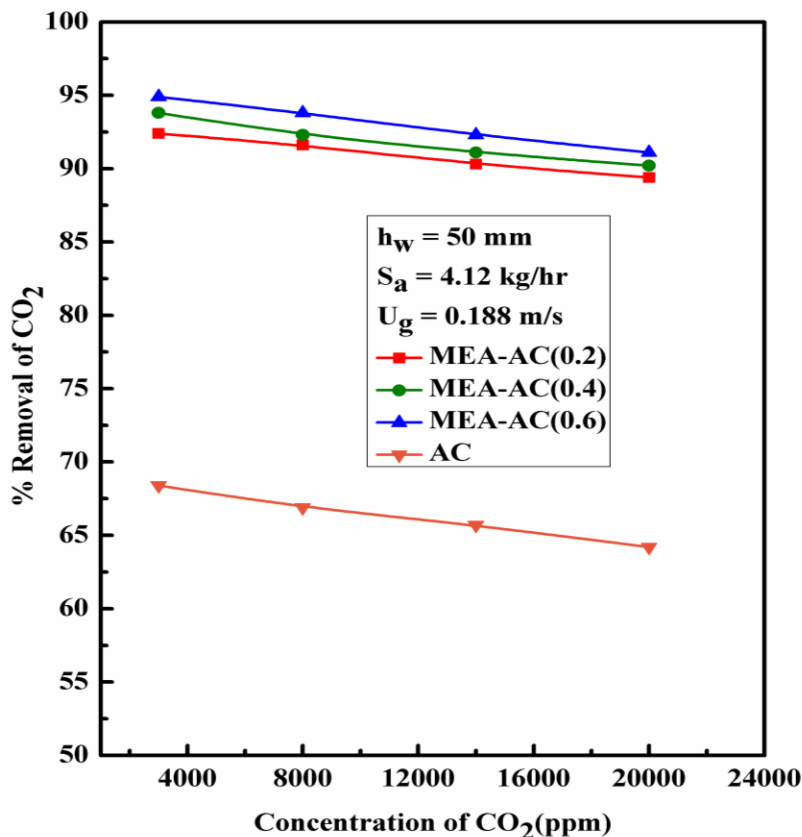
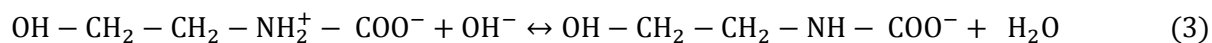
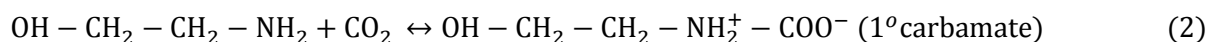


Fig. 4: Effect of impregnation ratio and comparison with AC

The explanation of MEA-AC has better removal capacity of CO₂ than AC and can be explained by the detailed Zwitterion mechanism, which is explained below.

4.2. Reaction Mechanism Chemistry

Zwitterion mechanism was originally proposed by Caplow, 1968 [14] and reintroduced by Danckwerts, 1979 [15]. It consists of a two-step mechanism i.e. the reaction between CO₂ and the amine proceeds through the formation of an intermediate called Zwitterion and the de protonation of the Zwitterion by a base. Fig. 5 shows the chemical structure of primary zwitterion ion. The actually reaction is shown below for MEA in presence of solvent water:



The rate determining step was the first reaction which results it into the formation of a primary carbamate ion for monoethanol amine solution. Stable carbamate ion leads to more forward side reaction and hence more adsorption (Das et al., 2016). The second step reaction occurs very fast in the presence of base. MEA is of less viscous that affects the CO₂ reaction to a greater extent. 1o amine was more stable and the main reason can be described because of the -I effect of one alcohol groups present in 1o amine. Hence the stability of 1o amine is more and thus MEA containing adsorbents shows greater adsorbent capacity.

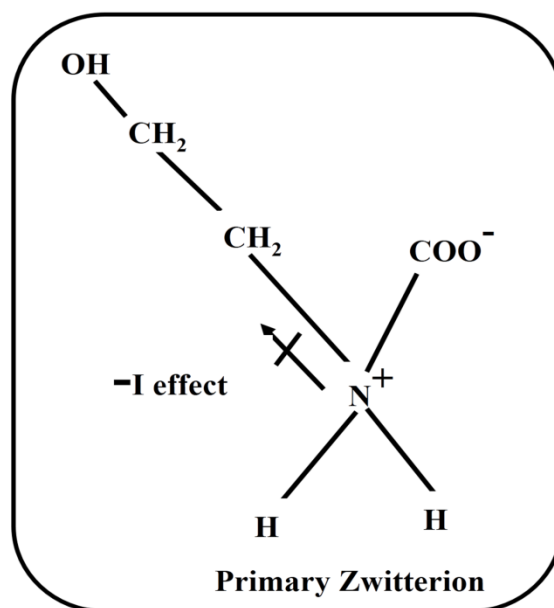


Fig. 5: Reaction mechanism of primary amine

5. Conclusion

The maximum % CO₂ removal occurs for MEA-AC (0.6) which led to 94.9 % removal under low gas flow rate. AC shows the minimum among the adsorbents due to only physical adsorption with CO₂. But in case of amine impregnated AC, both physical adsorption as well as chemical bonding between adsorbent and CO₂ occurs. The higher impregnation ratio leads to more removal of CO₂ because more amine functional groups are present in the activated carbon surface. 1o amine is more stable due to formation of stable carbamate ion. Zwitterions will be formed as a result of which there is more reactivity of the amine functional group with CO₂. So the adsorption capacity of AC < MEA-AC (0.2) < MEA-AC (0.4) < MEA-AC (0.6) was validated.

6. Acknowledgements

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7. References

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