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MARCH 18-19, 2015 DUBAI (UAE)

Editors:
Prof. Dr. Rahim Ahmadi
Prof. Dr. Mariam Gaidamashvili

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SECTION-II

Diethanolamine Functionalized Waste Tea Activated Carbon for CO_2 Adsorption

Manase Auta, Musa Umaru, Muibat Diekola Yahya, Olalekan David Adeniyi, Ibrahim Mohammed Aris, and Bilyaminu Suleiman

***Abstract*— Development of carbon (VI) oxide (CO_2) adsorbent was attempted by modifying mesoporous waste tea activated carbon (WTAC) with diethanolamine through impregnation. The modified and unmodified WTAC were used for selective adsorption of CO_2 from gaseous mixture (CO_2 and N_2). Effect of certain adsorption parameters such as concentration of the functionalizing agent (diethanolamine), column adsorption temperature, adsorbent dosage (bed height), concentration of the CO_2 in the feed and influent gas flow rate on breakthrough curves were evaluated. The exothermic nature of CO_2 capturing by MWTAC was physisorptive due to the increase in in adsorption at lower temperature and the extra amine groups present. The optimum condition for CO_2 capturing by MWTAC were at adsorption column temperature of 30 °C, 10 % CO_2 feed concentration, 1.0 M of diethanolamine used for modification and influent feed flow rate of 90 mL/min. The result of this investigation shows that MWTAC is an excellent CO_2-phylic adsorbent.**

***Keywords*— Adsorption, Carbon dioxide, Diethanolamine, Mesoporous activated carbon.**

I. Introduction

PROLIFERATION of fossil fuel exploration in on the rise due to increase in demand and consumers of the products. But the associated emission of CO_2 during the fossil fuel processing and usage impacts negatively on the pristine global climate. According to Fisher [1]., the use of fuel derived from coal, petroleum and natural gas for electricity generation and transportation purpose account for about 36% of CO_2 emission to the environment. The author further added that this source is the largest emitter of CO_2 to the atmosphere worldwide. Climate change, air toxics and ocean acidification are among the several other negative impacts faced with rise of CO_2 concentration in the entire ecosystem[2,3].

Several methods such as acqueous amine, adsorption, membrane separation, solid amine process amongst others have been employed for removing CO_2 from gaseous mixture. This is aside other measures like point source capture and sequestration processes put in place to alleviate its poisoning effect [1]. Among the numerous methods devised, adsorption stands out due to its simplicity, efficacy and affordability. The emergence of diverse adsorbents for capturing of CO_2 include examples of adsorbents like commercial activated carbons, molecular sieves, zeolite, clays amongst others have attracted investigation into the practicality, stability and design of full scale adsorption process [4]. More recently, efforts has been directed towards CO_2 capturing through functionalization of such adsorbents with amines, ammonia, base compounds and formation of composites [5]. This innovation has shown excellent CO_2 selectivity, high adsorption capacities and good adsorbent regeneration ability [2].

Amine modified adsorbents have been found to adsorb CO_2 molecules through chemical bond formation, pore diffusion, physical adsorption or physisorption (simultaneous physical and chemical) processes [6]. Chemical adsorption of CO_2 on amine (primary or secondary) modified sorbents principally gives rise to carbamate (thermally unstable due to its release of CO_2 at elevated temperature) and bicarbamate (further reaction of carbamate with CO_2 and water) [7]. In the presence of water molecules, stoichiometrically, one mole of CO_2 can chemically be bound to a mole of amine however, in dehydrated condition; a mole of CO_2 can adequately be chemisorbed on two moles of amine [3-4, 8-9]. To the best of the knowledge of the authors, there is no report on amine modified mesoporous waste tea activated carbon for CO_2 adsorption.

This research is aimed at synthesizing a cheap CO_2-phylic sorbent with high adsorption capacity by modifying mesoporous waste tea activated carbon with diethanolamine. The sorption capacity of different diethanolamine concentration was investigated and effect of column temperature, CO_2 feed concentration, Column adsorbent loading (bed-height) and feed flow rate on the breakthrough curves were examined.

II. Materials And Method

Carbon dioxide (99% purity) and Nitrogen gases were supplied by Whole sale gas company South Africa.

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Diethanolamine and methanol were supplied by Sigma-Aldrich Company in South Africa.

Preparation of adsorbent for CO_2 adsorption

Waste tea activated carbon (WTAC) was prepared as described in our previous work [10]. Modification of the WTAC with diethanolamine was carried out in a similar method used in our previous work [11].

Ten grams (10 g) of the WTAC was added to 300 mL of 1.0 M diethanolamine (28 mL of diethanolamine plus 300 mL of methanol) and stirred for 5 h at room temperature. The WTAC and amine mixture was washed with methanol after filtration and then dried under vacuum at 70 °C for 6 h. The dried WTAC modified with diethanolamine (MWTAC) was packaged in air tight container for further use.

Fixed-bed column adsorption

The column adsorption experiment of CO_2 with the MWTAC was carried out in a similar method as reported in our previous work [11]. The effect of some adsorption parameters such as concentration of diethanolamine used for modification (0.5 to1.5 M), percentage of CO_2 in the feed stream (10, 15 and 20%), gas influent flow rate (90, 120 and 150 mL/min), adsorbent dosage (2, 3 and 4 g) and column temperature (35, 45 and 55 °C) on the resulting CO_2 adsorption breakthrough curves were studied.

III. Results And Discussion

Effect of column temperature on breakthrough curves

The temperature at which the MWTAC adsorb CO_2 optimally connotes whether the adsorbent is suitable for pre or post-combustion effluent discharge processes. Breakthrough profiles with respect to temperature variation are presented in Fig. 1. The result of the investigation revealed that adsorption of CO_2 by MWTAC was favoured at low temperature of 30 °C; the adsorption capacities (mg/g) and breakthrough time (seconds) where 53.62, 34.27, 23.46 (mg/g) and 900, 605, 410 (s) for 30, 40 and 50 °C, respectively. This showed that modification of the WTAC with diethanolamine did not affect the adsorbent properties which were earlier reported demonstrating exothermic behavior towards liquid the adsorbate from the thermodynamic studies [12]. The exothermic nature of MWTAC adsorbent towards CO_2 is similar to that of silica-templated melamine-formaldehyde resin derived for CO_2 capture [13]. The reduction in CO_2 capture at elevated temperature by MWTAC was attributed to instability of the adsorbate molecules due to increase in excitement with addition of more heat to the system. The presence of extra amine groups on the adsorbent surface may have also contributed to the physisorption of CO_2 [14]. The physisorption nature of the CO_2 adsorption on MWTAC revealed that the adsorbent requires little or no extra energy before its active sites are activated to function optimally [15].

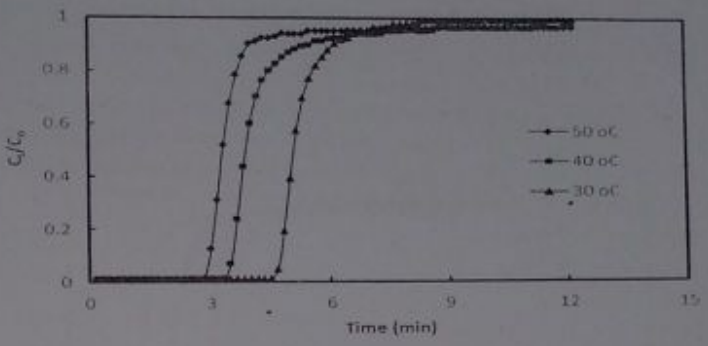

Fig.1 Adsorption column temperature variation effect on breakthrough curves at 10% CO_2 feed concentration (balance of N_2), 90 mL/min feed flow rate, 3 g adsorbent dosage, 1.0 M MWTAC particle sizes of 1-2 mm.

Effect of MWTAC adsorbent column loading on breakthrough curves

The breakthrough curves for the various masses of 1.0 M MWTAC were measured from the plot of C/Co (ratio of concentration of CO_2 in the fluid to that of the CO_2 in the influent feed) versus time. The effect of bed height on the breakthrough curves are presented in Fig. 2, at adsorbent column loading of 2, 3 and 4 g, the breakthrough time of 240, 900 and 970 s, and adsorption capacities of 19.83, 53.62 and 64.52 mg/g, respectively were obtained. The result of this study showed that high mass transfer was more pronounced at the inlet. This was obvious because the inlet point was the first point of contact between the inlet CO_2 gas and the adsorbent in the column. However, a gradual reduction in the mass transfer was observed with time as the sorbent became saturated [16]. At the breakthrough point, the adsorbent is saturated and the mass transfer zone (S-shaped) gradually moves away from the inlet until it attains equilibrium with the feed. It can be seen from Fig. 2 that the more the mass (bed height) of the 1.0 M MWTAC used in the column, the longer the breakthrough time and adsorption capacity. This observation is in accordance with the expected trend [17].

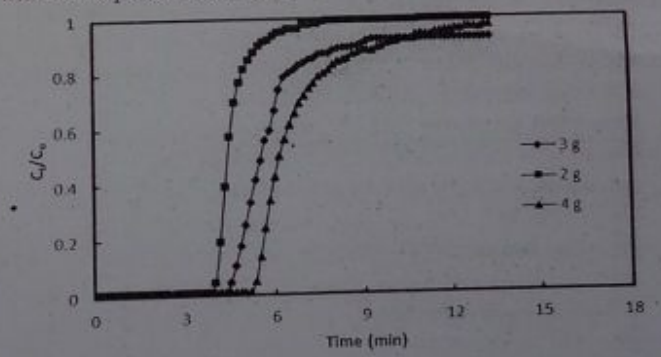

Fig. 2 Adsorbent dosage (bed-height) effect on breakthrough curves at 10 % CO_2 feed concentration (balance of N_2), 90 mL/min feed flow rate, 3 g adsorbent dosage, 1.0 M MWTAC particle sizes of 1-2 mm, 30 °C adsorption column temperature.

Effect of feed flow rate on breakthrough curves

Variation of feed flow rate was directly proportional to the quantum of the gas molecules contacted the surface of the MWTAC adsorbent. The resultant profiles of the flow rate

variation are shown in Fig. 3. Rapid attainment of breakthrough point (135 s) was observed at high feed flow rate (150 mL/min) which was attributed to fast preponderance of numerous molecules contact to the static or inelastic vacant sites of the adsorbent. Whereas, gradual and longer time of breakthrough point (900 s) attainment was associated with the low feed flow rate (90 mL/min). Low feed flow rate may have created or given room for ample residence time thereby enabling chronological adsorption of CO_2 molecules enormously. It has also been observed by other researchers also that concurrent reduction of CO_2 adsorption and breakthrough time occurs at higher influent flow rate of the gas [18].

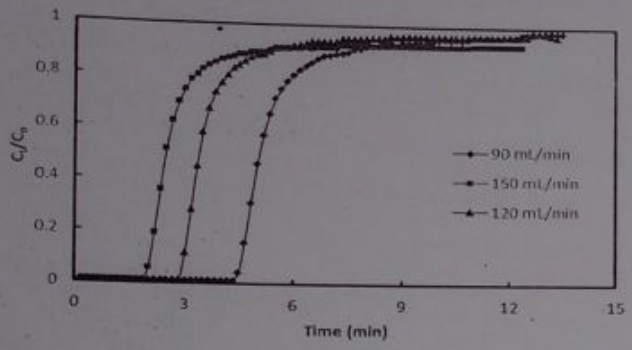

Fig. 3 The effect of Feed flow rate variation on breakthrough curves at 10% CO_2 feed concentration (balance of N_2), 3 g adsorbent dosage, 1.0 M MWTAC particle sizes of 1-2 mm, 30 °C adsorption column temperature

Effect of diethanolamine concentration used for modification on the adsorbent activities

Adsorption activities of the unmodified and modified waste tea activated carbon were evaluated for CO_2 capturing and the breakthrough profiles of the evaluation are presented in Fig. 4. The use of 0.5, 1.0 and 1.5 M diethanolamine functionalizing agent for modification and use of un-functionalized adsorbent (UMWTAC), gave corresponding adsorption capacities of 33.57, 53.62, 46.23 and 20.07 mg/g, respectively. The modified waste tea activated carbon with diethanolamine (MWTAC) adsorbent, exhibited longer breakthrough curves and better adsorption of the CO_2 than the unmodified waste tea activated carbon (UWTAC). The introduction of the extra amine groups on the WTAC surfaces enhanced attraction of the negative CO_2 molecules to the adsorbent surface. However, inadequate (0.5 M diethanolamine) and outrageous (1.5 M diethanolamine) concentration of the functionalization agent impeded adequate CO_2 adsorption. The presence of larger amine molecules at higher concentration may have affected the WTAC surface area thereby reducing the adsorption activity area. On the contrary, inadequate availability of the amine molecules on the WTAC surface to increase the vacant active sites may not had measured up the available and numerous CO_2 adsorbate molecules available for adsorption. The increase in CO_2 adsorption observed with 1.0 MWTAC adsorbent was attributed to even distribution of the molecules of the functionalization agent on the adsorbent surface in a proportionate manner. The amount of CO_2 adsorbed by these adsorbent was in this order 1.0 MWTAC > 1.5 MWTAC > 0.5 MWTAC > UWTAC. The clear distinction and better adsorption observed with amine modified adsorbent (MWTAC) was attributed to dual (chemical and physical) sorption through formation of bicarbonate and carbamate and, perineation of CO_2 molecules to the pores; unlike the UWTAC adsorption that was probably physically based [3,18].

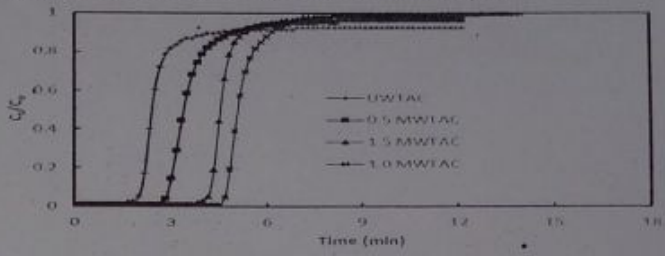

Fig. 4 Effect of functionalization agent (diethanolamine) concentration on breakthrough curves at 10 % CO_2 feed concentration (balance of N_2), 90 mL/min feed flow rate, 3 g adsorbent dosage, 1.0 M MWTAC particle sizes of 1-2 mm, adsorption column temperature of 30 °C.

Effect of the CO_2 feed concentration on the breakthrough curves

The concentration of CO_2 in the feed determined the available flow of the adsorbate molecules that interacted with the active site on the fixed adsorbent surface. The level of electrostatic attraction between the active sites of the adsorbent surface and the adsorbate molecules informed the suitability of the CO_2 feed concentration adequate for adsorption. The effect of the initial CO_2 feed concentration variation on the breakthrough point is presented in Fig. 5. The Fig. 5 revealed that 10 % CO_2 concentration in the feed at 90 mL/min was most suitable for the adsorption study as it recorded an adsorption capacity of 53.62 mg/g and 900 s breakthrough time. This was evident in the longer breakthrough curves and higher adsorption capacity that resulted. However, further increase in the initial CO_2 feed concentration (15 to 20 %) resulted in the reduction of the MWTAC adsorption capacity (50.70 and 46.84 mg/g at 580 and 530 s, respectively). This may be attributed to overwhelming and poor attraction of the adsorbent active sites when larger numerous CO_2 molecules were available for uptake.

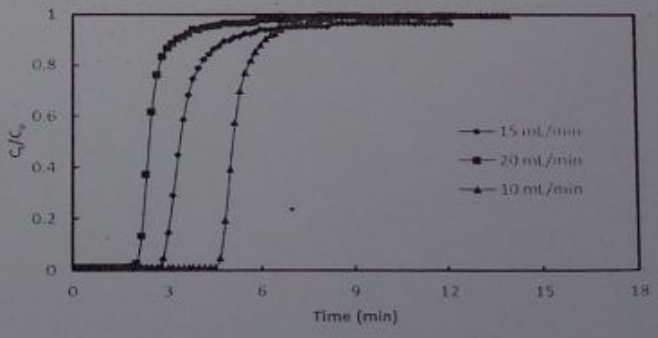

Fig. 5 Effect of CO_2 feed concentration on breakthrough curves at 30 °C adsorption column temperature, 90 mL/min feed flow rate, 3 g adsorbent dosage, 1.0 M MWTAC particle sizes of 1-2 mm.

IV. Conclusion

Modification of mesoporous waste tea activated carbon with diethanolamine was successfully carried out and used for the adsorption of carbon dioxide from gaseous mixture. (CO_2 and N_2). The 1.0 M MWTAC adsorbent removed CO_2 from the fluid in both physical and chemical processes (physisorptive). The optimum conditions for adsorbing CO_2 were at adsorption column temperature of 30 °C, 10 % CO_2 feed concentration, 90 mL/min influent fluid flow rate, 3 g adsorbent (1-2 mm particle sizes) dosage.

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