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Carbon dioxide capture using bi-blended and tri-blended amines solution in packed bed absorber

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Abstract

Carbon capture and storage technologies are crucial in mitigating greenhouse gas emissions. This study investigates the enhancement of CO_2 absorption through refining amine blends, specifically diethylenetriamine (DETA) with monoethanolamine (MEA) and tetraethylenepentamine (TEPA) with MEA at different concentrations and employing chemical promoters to boost the performance of the gas treatment system. The behaviour of these amines was evaluated by the impact of mixing DETA and MEA across different concentrations. The results showed that the removal efficiency increased with increasing DETA concentration. Similarly, the TEPA-MEA blend was investigated, demonstrating an increase in removal efficiency with increasing TEPA concentration. Removing efficiency improved from 75% with 30% MEA to about 96% with a 15% MEA and 15% TEPA mixture while maintaining the absorption rate due to the sufficient column height. Also, the study explores the effect of utilizing chemical promoters, specifically piperazine (PZ), potassium carbonate (K_2CO_3), and benzylamine (BZ), when combined with 15 % MEA and 10% DETA to boost the absorption rate and improve the CO_2 loading capacity. The findings indicate that adding 5% BZ to the MEA-DETA solution increases removal efficiency by 10%. Moreover, adding 5% PZ to the same mixture increased efficiency by about 18%. Meanwhile, the volumetric mass transfer coefficient, KGav, more than doubled. Finally, the study examined the effect of using the same promoters with 15% MEA and 10% TEPA on CO_2 capacity and mass transfer rates. The outcomes demonstrate that both removal effectiveness and KGav were dropped when using BZ and K_2CO_3 in the MEA-TEPA blend. The removal efficiency increased somewhat with PZ, but KGav was not significantly affected. In conclusion, the mass transfer rate and CO_2 removal efficiency from flue gases will be enhanced by the use of bi-amines such as MEA-DETA and MEA-TEPA in chemical absorption. However, because they enhance the amine group in the absorbent, promoters such as PZ and BA can raise the carbon dioxide removal efficiency to an economically valuable level.

Keywords: Amine absorption; CO_2 removal; Packed bed absorption; amines promoter; piperazine; benzylamine.

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1- Introduction

The world's energy consumption has increased significantly due to the sudden increase in global population and tremendous industrial advances; however, traditional energy sources like petroleum are responsible for animal harm, air and water pollution, and various other problems when employed [1]. Carbon dioxide is the primary greenhouse gas responsible for global warming [2-3]. The "greenhouse effect" phenomenon is caused by greenhouse gases [4]. Terms related to the greenhouse effect describe the warming of the Earth's surface caused by solar radiation mainly passing through the atmosphere unmodified [5]. After being released once more as infrared radiation, the majority of the energy is absorbed by carbon dioxide and water vapor in Earth's atmosphere, which envelops the globe like a blanket [6]. Because of our continued reliance on fossil fuels, the atmosphere's carbon dioxide concentration is increasing each year, exacerbating the planet's greenhouse effect [7].

According to the United Nations Development 2030 Agenda, annual global greenhouse gas emissions reached 50 billion tons of carbon dioxide equivalents (CO_2) in 2019, i.e., around 6.6 tons of CO_2 per capita. In 2021, global emissions have almost recovered to their pre-pandemic peak. At the worldwide level in 2019, the top 10% of global emitters (771 million individuals) emit, on average, 31 tons of CO_2 per person per year and are responsible for about 48% of global CO_2 emissions. The bottom 50% (3.8 billion individuals) emit an average of 1.6 tons each and account for nearly 12% of total emissions. The global top 1% emits, on average, 110 tons and accounts for 17% of all emissions. Therefore, reducing atmospheric CO_2 concentrations may help minimize global warming and its effects on climate change [8-9]. One strategy to reduce CO_2 emissions from burning fossil fuels is to use carbon capture and storage (CCS) [2]. To implement CCS, concentrated CO_2 streams from specific sources—such as factory exhaust

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emissions—must be captured. These streams must then be securely stored in an appropriate geological reservoir. Examples of reservoir geological structures are saline aquifers, inaccessible coal seams, and drained oil or gas reservoirs [10]. Many techniques, such as cryogenic, membrane, gas separation, absorption, and adsorption, are available to capture carbon dioxide [3]. The most modern and practical method for lowering carbon dioxide emissions from large fossil fuel-powered plants is post-combustion capture (PCC), which uses the chemical capture strategy, namely amine solution absorption [11]. These methods of separation could selectively remove CO_2 from gas mixtures by using absorption scrubbers, which typically employ packed-bed absorbers because gaseous carbon dioxide reacts rapidly with amine solutions [12].

In recent decades, in response to climate change, the demand for effective carbon capture technologies has grown. Several solvents have been utilized in the carbon capture processes. Among these solvents, monoethanolamine (MEA), known for its higher absorption rates, has been traditionally used as the leading choice in carbon capture systems [13]. Researchers have looked into combining different amines to enhance the functionality of the traditional solvent (MEA) [14]. Since polyamines comprise numerous amino groups in a single molecule, with high reaction rates and high CO2 loading capacity for CO_2 capture, their interest in CCS procedures has grown significantly [15].

Researchers are seeking new chemical solvents to use in combination with standard monoethanolamine (MEA) or as an alternative to MEA to enhance the overall effectiveness of carbon dioxide absorption. To optimize the advantages of each amine and improve the overall performance of the chemical absorbent, blending several amines is a wise choice [16]. Xu et al. (2016) experiments were carried out in a packed bed absorber using 1- 4 kmol/m^3 of MEA, MDEA, and DEEA as a chemical absorbent, showing that: The K_Ga_v increases with liquid input temperature, liquid flow rate, and amine concentration; it decreases with increasing carbon dioxide loading and is largely unaffected by inert gas flow rate. Compared to MDEA, DEEA has a higher K_Ga_v value; however, it is lower than MEA. In terms of K_Ga_v and cyclic capacity, structured packing performs better than random packing. Due to their distinct forms, in which each molecule contains multiple amine groups such as diethylenetriamine (DETA) and triethylenetetramine (TETA), one type of amine absorbent that shows promise is polyalkanol amine, which has strong reaction kinetics and thermodynamic capabilities [17]. Al-Sudani carried out experimental investigations in a ceramic Rashing ring-packed bed absorber utilizing a blended alkanol amine absorbent comprising MEA and PZ, NH_3, with a total concentration of 0.3-0.7 kmol/m^3. Her experimental investigations' results show that, under varied operating circumstances, increasing absorbent flow rates and inlet carbon dioxide partial pressures increased K_Ga_v values. Furthermore, the average KGav values first rise and then fall beyond the gas flow rate when the gas flow rate increases by 10 liters per minute.

This study mainly focuses on a comparative examination to compare the effectiveness of CO_2 absorption through the use of the blending of the amine performance as a solvent and promotes these bleedings with additives using the same experimental setup with various mass blending ratios; the demonstration is investigated Concerning the overall mass transfer coefficient (KGav); sweet CO_2 concentration and carbon dioxide removal efficiency (η).

2- Analytical study

2.1. Volumetric coefficient of mass transfer (KGa_v)

The packed absorption efficiency per unit volume is represented by the lumped parameter, the overall mass transfer coefficient (KGav). The three parameters for the carbon dioxide absorption system's mass transfer are kinetics, hydrodynamics, and thermodynamics. It is an important parameter since it may be used to calculate the height of the absorber column [18]. When carbon dioxide crosses the gas-liquid boundary into the liquid phase, mass transfer occurs. The two bulk phases of mass transfer are an, where the gas side is the flue gas and the fluid side is the amine solution [19]. Eq. 1 can be used to compute the overall carbon dioxide flow, N_CO$_2$, across the gas-liquid interface from the gas bulk to the liquid bulk, using the two-film theory. The driving force in Eq. 1 is denoted by the distinction between the bulk gas side mole fraction of CO_2 (y_{CO2}) and the bulk liquid side equilibrium concentration of CO_2 (y^*_{CO2}) [20].

$$N_{CO2} = KG * P * (y_{CO2} - y^*{}_{CO2}) \quad (1)$$

where P is the operating pressure and KG is the overall mass transfer coefficient, mass transfer based on the gas phase; as a result:

$$KG = \frac{N_{CO2}}{P(y_{CO2} - y^*{}_{CO2})} \quad (2)$$

KGa_v can be obtained by employing Eq. 2 by multiplying it by the term of interfacial area $\frac{a_v}{a_v}$ as follows:

$$KG = \frac{N_{CO2}}{P(y_{CO2} - y^*{}_{CO2})} * \frac{a_v}{a_v} \quad (3)$$

Simplifying Eq. 3 to get Eq. 4

$$KG * a_v = \frac{N_{CO2}}{P*(y_{CO2} - y^*{}_{CO2})} * a_v \quad (4)$$

The term N_{CO2} av can be computed from the carbon dioxide concentration profile measured in a packed section of the absorber, as demonstrated experimentally by Naami et al. [19]. In accordance with Fig. 1, mass balancing based on carbon dioxide is performed over this slice, assuming a component of height dZ along the absorber-packed section. One way to express the resulting equation is as follows [19]:

$$N_{CO2}\, a_v * dZ = G * d\left(\frac{y_{CO2}}{(1-y_{CO2})}\right) \quad (5)$$

The CO_2 molar ratio in the bulk gas phase is represented by $\frac{y_{CO2,}}{(1-y_{CO2})}$, which can also be expressed as Y_{CO2}. A differential height section of the packing is denoted by dZ, and the total molar flow of the untreated gas without carbon dioxide flow is shown by G. An alternative way to express Eq. 5 is as follows:

$$N_{CO2} = \frac{G}{a_v dZ} * d(Y_{CO2}) \quad (6)$$

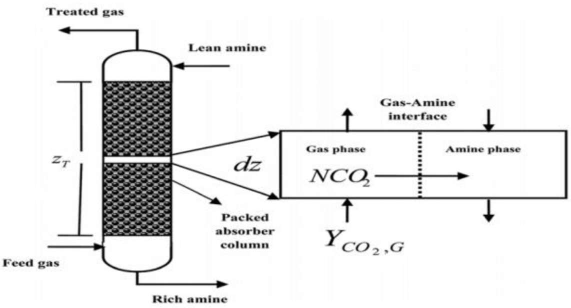


Fig. 1. The mechanism of CO_2 absorption mass transfer

Eq. 6 can then be applied in conjunction with Eq. 4 as seen below:

$$KG * a_v * \left(y_{CO2} - y^*_{CO2}\right) * P * dz = G * dY_{CO2} \quad (7)$$

Rearrangement Eq. 7 to get Eq. 8

$$KG * a_v = \frac{G}{P*(y_{CO2} - y^*_{CO2})} * \left(\frac{dY_{CO2}}{dz}\right) \quad (8)$$

Since the reaction scheme's immediate mechanism is satisfied by carbon dioxide chemisorption within the alkanolamine absorbent. Afterwards, y^*_{CO2} achieves zero in the absence of CO_2 mole fraction at the liquid phase. The equilibrium CO_2 mole fraction in the bulk gas phase is related to the CO_2 mole fraction in the liquid bulk phase, which is denoted by the word y^*_{CO2} [21].

$$KGa_v = \frac{G}{P*\int_0^Z dz} * \int_{Y1}^{Y2}\left(\frac{1}{y_{CO2}}\right) dY_{CO2} \quad (9)$$

Since,

$$Y_{CO2} = \frac{y_{CO2}}{1-y_{CO2}} \quad (10)$$

To obtain the central equation that determines the overall mass transfer coefficient (KGa_v), one can substitute Eq. 10 into Eq. 9 and integrate Eq. 9 for all variations in the CO_2 molar ratio along the height of the packing section. This results in the following equation.

$$KGa_v = \frac{G}{P*Z} * \left[\ln\left(\frac{y_{CO2,in} *(1-y_{CO2,out})}{y_{CO2,out} *(1-y_{CO2,in})}\right) + \left(\frac{y_{CO2,in}}{(1-y_{CO2,in})} - \frac{y_{CO2,out}}{(1-y_{CO2,out})}\right)\right] \quad (11)$$

where Z is the packing height, y_{CO2in} is the CO_2 concentration at the inlet, and y_{CO2out}) is the CO_2 concentration at the outlet.

2.2. Determination of CO_2 removal efficiency

The amount of carbon dioxide absorbed by an alkanol amine solvent is known as the carbon dioxide capture efficiency (η). Here is the equation for this [18]:

$$\eta = \left(1 - \frac{y_{CO2,out}}{1-y_{CO2,out}} * \frac{1-y_{CO2,in}}{y_{CO2,in}}\right) * 100\ \% \quad (12)$$

3- Experimental work

3.1. Materials

Monoethanolamine (MEA, Thomas Baker, >98%); Diethylenetriamine (DETA, Fluka, >97%); Triethylenetetramine (TEPA, Fluka, >97%): The chemicals employed in this experiment are listed below, together with additional information on their molecular weight, business name, physical state, and purity, as indicated in Table 1. Hydrochloric acid (HCl, CDH, 35-38%), distilled water, CO_2 gas cylinder (>99.6 vol.%), and N_2 gas cylinder (>99.8 vol.%) were supplied by Albilal Gas Company, located in Baghdad, to prepare the absorbate gas mixture. All amine solutions were made with purified water and volumetric glassware, and the components were utilized exactly as received. Experimental absorption system.

This experiment used the absorption pilot depicted in Fig. 2. The packed column, measuring 1.8 meters in height and 40 millimeters in diameter, makes up the majority of this unit. It is divided into 5 packed stages, with a side stream drawn from each stage; Table 3 lists all the absorber tower design specifications. The ceramic Intalox saddle type fills the packed column. The Experimental Operating Conditions range is provided in Table 2. The column is composed of acrylic, and the ceramic packing material is arranged randomly. The operation was performed in continuous mode, which ensured countercurrent flow and improved CO_2 chemical absorption through precise diffusion to both the gas and liquid phases.

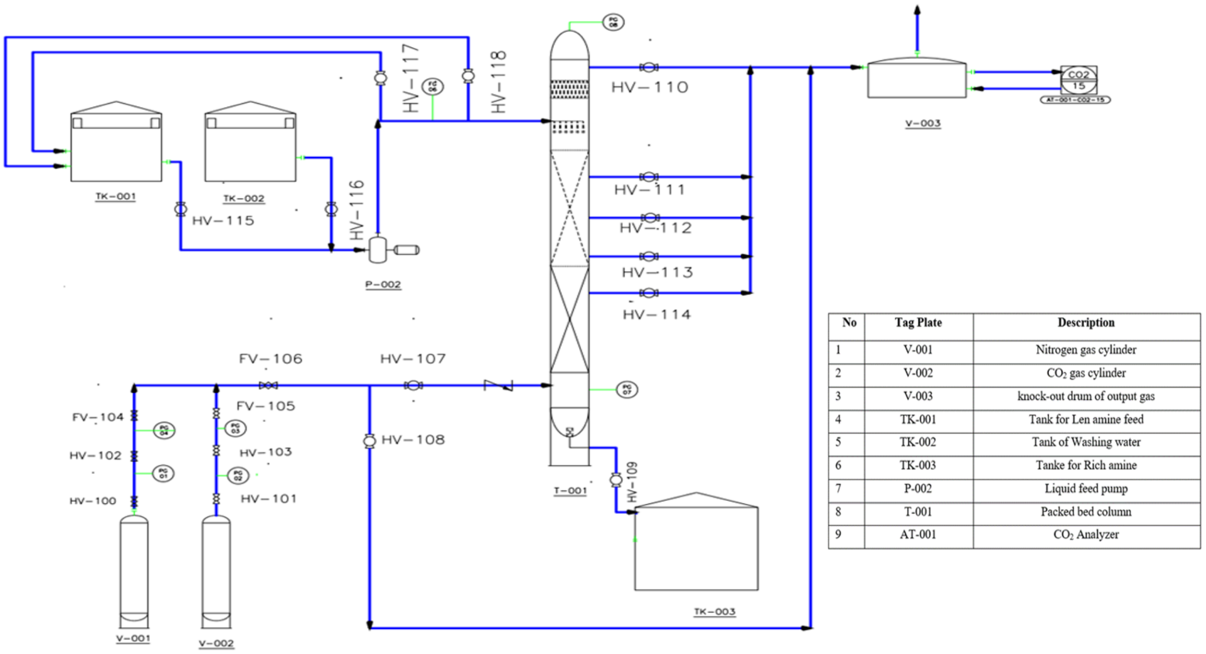
The liquid phase was fed from the top, and gravity brought it all the way down to the base of the packed column, while the gas phase was continually fed into the column from its base and followed up. Once the amine solution had been heated to the proper operating amine temperature on the hot plate magnetic stirrer (Dragon Lab, Australia), it was immediately transferred into the packed reactor using a diaphragm pump (TYP-2500NH, China). For every test, a 500-cc amine solution is employed. The amount of carbon dioxide in the effluent gas was measured using an inline CO_2 gas analyzer (BIOGAS 5000, UK). Two separate gas flow meters (Bass Instrument, Turkey) with a range of 0 to 10 L/min were used to construct the feed-simulated gas mixture simulated gas mixture was first added to the CO_2 analyzer to measure its concentration. The gas analyzer's readout of carbon dioxide content confirms that the absorption process continues until the absorption rate no longer changes (steady-state operation).

3.2. Experiment operation procedure

The operating procedure will be divided into several stages, from solvent preparation through shutdown. All operation stages will be discussed in detail below, with the operating sequence illustrated in Table 3 and Fig. 2, and the prepared solutions with mixing ratios for each experiment are listed in Table 4.

Table 1. Experimental materials and chemical

No	Materials	Chemical structure	Company	Origin Century	M.wt g/mol	Purity / State
1	Monoethanolamine	C_2H_7NO	Thomas Baker	India	61.08	97 % Liquid
2	Tetraethylenepentamine	$C_8H_{23}N_5$	Fluka		189.3	97 % liquid
3	Benzylamine	C_7H_9N			107.1	96 % liquid
4	Hydrochloric acid	HCl	CDH	India	36.46	35-38% Liquid
5	Piperazine	C4H10N2			86.14	99.1% solid
6	Potassium carbonate	K2CO3			138.21	99.2% solid
7	Carbon dioxide	CO_2	AL-Nahrawan Gas Company	Iraq	44.01	99.6 % purity gas
8	Nitrogen	N_2			28.02	
9	Pure water	H_2O	Dep Lab.Fluka	Iraq	18	TDS=5 ppm PH=6.99 Cond.=10µs/cm



No	Tag Plate	Description
1	V-001	Nitrogen gas cylinder
2	V-002	CO_2 gas cylinder
3	V-003	knock-out drum of output gas
4	TK-001	Tank for Len amine feed
5	TK-002	Tank of Washing water
6	TK-003	Tanke for Rich amine
7	P-002	Liquid feed pump
8	T-001	Packed bed column
9	AT-001	CO_2 Analyzer

Fig. 2. Process flow diagram of absorption unit experimental setup

Table 2. Experimental operating conditions range

Absorbent	Operating conduction	Variable parameter
MEA-DETA	T=298 K, P=1 bar, L=20mi/min, amine= 30 wt%, G=6 LPM, co2=15 mol%,	DETA=5,10,15 WT %
MEA-TEPA	T=298 K, P=1 bar, L=20mi/min, amine = 30 wt%, G=6 LPM, co2=15 mol%,	TEPA =5,10,15 WT %
MEA-DETA-promoters	T=298 K, P=1 bar, L=20mi/min, amine = 30 wt%, G=6 LPM, co2=15 mol%,	Pz=5 wt% ,BZ=5 wt % k2co3 =5 wt %
MEA-TEPA-promoters	T=298 K, P=1 bar, L=20mi/min, amine = 30 wt%, G=6 LPM, co2=15 mol%,	Pz=5 wt%, BZ=5 wt %, k2co3 =5 wt %

4- Results and discussion

4.1. Amines blends

This section aims to provide extensive data collection from studies conducted in a lab-scale packed column under various process circumstances, focusing on carbon dioxide absorption into aqueous mixed DETA or TEPA with MEA absorbent.

Table 3. Operating sequence steps: C=Close, O=Open

Manual valves	**HV 102**	**HV 103**	**HV 106**	**HV 107**	**HV 108**	**HV 109**	**HV 110**	**HV 111**	**HV 112**	**HV 113**	**HV 114**	**HV 115**	**HV 116**	**HV 117**	**HV 118**
Washing	C	C	C	C	C	O	C	C	C	C	C	C	O	C	O
Purging with N_2	O	C	O	O	C	C	O	O	O	O	O	C	C	C	C
Liquid Flow calibration	C	C	C	C	C	C	C	C	C	C	C	O	C	O	O
Set inlet CO_2 concentration	O	O	O	C	O	C	C	C	C	C	C	C	C	C	C
Startup from the top stream	O	O	O	O	C	O	O	C	C	C	C	O	C	O	C
Startup from 2nd side stream	O	O	O	O	C	O	C	O	C	C	C	O	C	O	C
Startup from 3rd side stream	O	O	O	O	C	O	C	C	O	C	C	O	C	O	C
Startup from 4th side stream	O	O	O	O	C	O	C	C	C	O	C	O	C	O	C
Startup from bottom-side stream	O	O	O	O	C	O	C	C	C	C	O	O	C	O	C

Table 4. Operating runs at different amines blends and promoters

Amine solvent for each run	**Amine concentration Wt %**	**Amine solvent for each run**	**Amine concentration Wt %**
MEA-DETA	25 MEA, 5 DETA	MEA-DETA-BZ	15 MEA,10 DETA,5 BZ
MEA-DETA	20 MEA, 10 DETA	MEA-DETA-PZ	15 MEA,10 DETA,5 PZ
MEA-DETA	15 MEA, 15 DETA	MEA-DETA-K_2CO_3	15 MEA ,10 DETA,5 K_2CO_2
MEA-TEPA	25 MEA,5 TEPA	MEA-TEPA-BZ	15 MEA,10 TEPA, 5 BZ
MEA-TEPA	20 MEA,10 TEPA	MEA-TEPA-PZ	15 MEA,10 TEPA,5 PZ
MEA-TEPA	15 MEA,15 TEPA	MEA-TEPA-K_2CO_3	15 EA,10 TEPA,5 K_2CO_3

a. MEA and DETA blending

Diethylenetriamine (DETA) outperformed other alkanol amines, as demonstrated by the preceding sections. As a result, diethylenetriamine can be used as an activator with the traditional monoethanolamine (MEA) absorbent to improve carbon dioxide capturing performance. In actual applications, operating conditions affect carbon dioxide capture performance and the absorbent type. In an absorption column randomly packed with diethylenetriamine (DETA) solutions, the mass-transfer performance of CO_2 absorption was studied and compared with that of monoethanolamine (MEA), a commonly used benchmark solvent for CO_2 absorption [22].

The single-amine behaviour of these blends has been contrasted with that of DETA-MEA mixtures at various concentrations. A novel blend is employed at varying concentrations: 25% MEA with 5% DETA, 20% MEA with 10% DETA, and 15% MEA with 15% DETA, compared with earlier runs of 30% MEA and 30% DETA individually. The CO_2 removal efficiency increased by 10% when the DETA concentration rose from 5% to 15%. Compared with ordinary amines, DETA, a polyamine containing two primary and one secondary amine group, has a larger absorption capacity and a faster response rate [23]. The results are recorded and analyzed to determine the removal efficiency and mass transfer coefficient.

Fig. 3 and Fig. 4 demonstrate that the removal efficiency increases as the solvent mixture's DETA concentration increases. Because DETA contains several amine groups, increasing the CO_2 capacity of amine compounds enhances the solvent capacity for amines. Hadri et al [24]_provided evidence about the effect of the α-substituent type (alkyl or alcohol group) on the loading capacity. It was shown that whereas the alkyl substituent boosted absorption capacity, the -OH group negatively impacted the CO_2 absorption rate. The results showed that basicity increased with increasing carbon chain length. As this researcher explains, the electron density at the nitrogen atom in the nitrogen molecule is reduced due to the -OH group's electron-withdrawing effect. Consequently, the -OH group's electron-withdrawing function is decreased when the distance between the amine group and the -OH group is increased, which promotes amine protonation and increases the basicity of the alkanolamine [25].

It's also important to keep in mind that adjusting the weight percentage of combined amine solvents is trickier than it is for individual solvents. The reasoning is that adding too much amine or water to the mixture changes the weight percent of each amine solvent in the aqueous amine solution, thereby reducing the carbon dioxide loading capacity. The optimum amount of the aquatic amine liquid provides 90% CO_2 capture efficiency [26].

Since the column height is sufficient, Fig. 5 shows KGav as a function of column height, which also increases with increasing DETA concentration. Since DETA has more carbon atoms than MEA, which decreases the solubility of CO_2 in this amine blend, an increasing concentration of DETA of more than 50% causes a drop in the amine blend's solubility and lowers the physical absorption rate. Fig. 6 shows the KGav for Individual packing bed performance, indicating which layer has a lower mass transfer rate and higher resistance. The bi-solvent mix's goal, initially proposed by Chakravarty et al. (1985), is to minimize each amine solvent's unique issues while optimizing its potential.

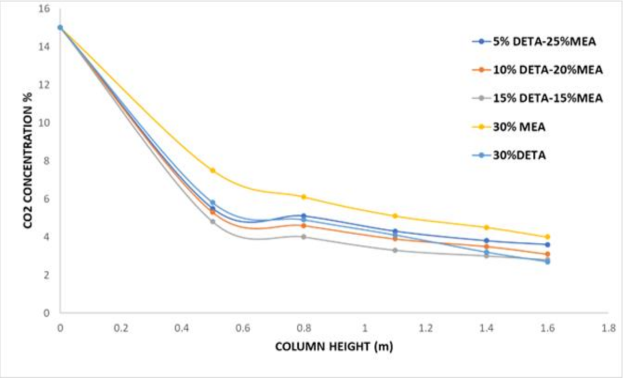


Fig. 3. Carbon dioxide concentration of MEA-DETA system along the packed bed column at 6 LPM gas flow rate with 15 mole % CO2, 20 ml/ min of amine with 30wt% concentration, T=298K, and P=1 bar

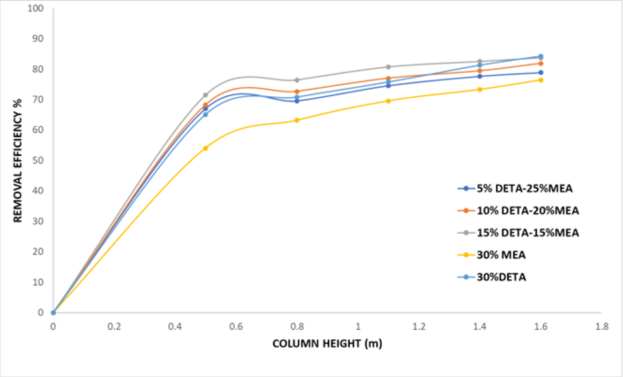


Fig. 4. Carbon dioxide removal efficiency of MEA-DETA system along the column height at 6 LPM gas flow rate with 15 mole % CO_2, 20 ml/ min of amine with 30wt% concentration, T=298K, and P=1 bar

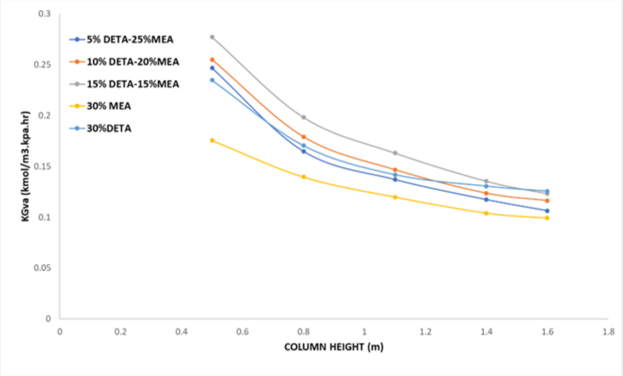


Fig. 5. Volumetric mass transfer coefficient for MEA-DETA along column length at 6 LPM gas flow rate with 15 mole % CO_2, 20 ml/ min of amine with 30wt% concentration, T=298K and P=1 bar

Bi-solvent blends typically combine a highly reactive amine solvent with a solvent with a high capacity to absorb CO_2. The solvent with a high capacity for CO_2 absorption (i.e., an equilibrium CO_2 loading of at least 1 mol CO_2/mol amine) is frequently a tertiary or sterically hindered amine because amines can produce bicarbonates (HCO_3) during amine CO_2 reactions. The two forms of reactive amine solvents are reactive monoamines (primary and/or secondary amines) and polyamines with primary and/or secondary amino groups that can form stable carbamates [26].

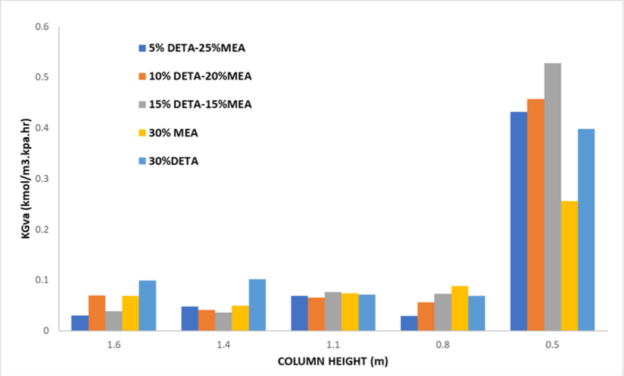


Fig. 6. Volumetric mass transfer coefficient for MEA-DETA for each stage of packing bed at 6 LPM gas flow rate with 15 mole % CO_2, 20 ml/ min of amine with 30wt% concentration T=298K, and P=1 bar

b. MEA and TEPA blending

The single-amine behavior of these blends has been contrasted with that of TEPA/MEA blends at various concentrations. A novel blend is employed with varying concentrations: 25% MEA with 5% TEPA, 20% MEA with 10% TEPA, and 15% MEA with 15% TEPA, compared with earlier runs of 30% MEA and 30% TEPA individually. The mass transfer coefficient and removal efficiency are calculated by recording and analyzing the data. Fig. 7 and Fig. 8 demonstrate that the removal efficiency increases as the solvent mixture concentration increases. Since TEPA includes many amine groups, increasing the CO_2 capacity of amine compounds leads to a rise in the amine solvent capacity. Because it has five amine groups in its structure, the removal effectiveness has risen from 75% at 30% MEA utilization to about 96% at 15% MEA and 15% TEPA, without affecting the absorption rate, since the height is sufficient.

The study's findings demonstrated that the steric hindrance in branched-chain alkanol amines produced significantly faster desorption rates, higher CO_2 solubility and cyclic capacity, and substantially lower heat duty for solvent regeneration compared to their straight-chain counterparts. However, there was only a slight decrease in the carbon dioxide absorption rate [25].

Fig. 9 and Fig. 10 depict the KGav along the column height. Since the column height is sufficient, the removal efficiency is likewise boosted with increasing TEPA concentration. Since TEPA has more carbon atoms than MEA, which decreases the solubility of CO_2 in this amine blend, an increasing TEPA concentration of more than 50% causes a drop in the solubility of the amine blend and reduces the physical absorption rate. The findings demonstrated that as the length of the carbon chain increased, basicity increased [25].

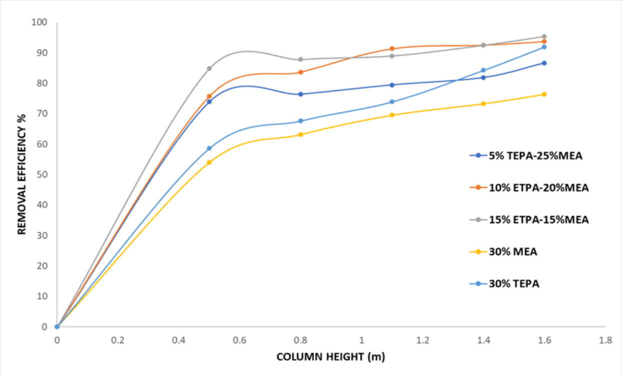


Fig. 7. Carbon dioxide removal efficiency of MEA-TEPA system along the column height at 6 LPM gas flow rate with 15 mole % CO_2, 20 ml/ min of amine with 30wt% concentration, T=298K, and P=1 bar

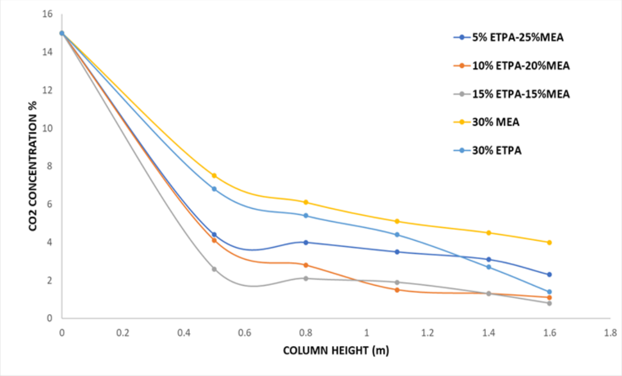


Fig. 8. Carbon dioxide concentration of MEA-TEPA system along the column height at 6 LPM gas flowrate with 15 mole % CO_2, 20 ml/ min of amine with 30wt% concentration T=298K and P=1 bar

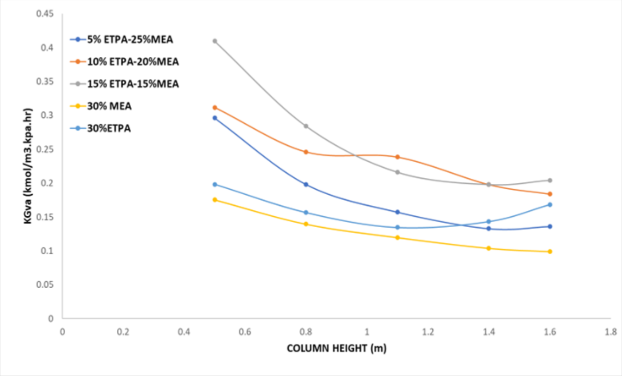


Fig. 9. Volumetric mass transfer coefficient for MEA-TEPA along the column length at 6 LPM gas flowrate with 15 mole % CO_2, 20 ml/ min of amine with 30wt% concentration T=298K and P=1 bar

4.2. Promoters to amines blends

a. Promoters with DETA -MEA- mixture

Prompters such as PZ, K_2CO_3, and benzylamine (BZ) are investigated by blending it with 15 % MEA and 10% DETA to enhance bendings amines' absorption rate and CO_2 capacity. It was discovered that piperazine (PZ) in an aqueous solution had low volatility, a high reaction rate, and little equipment corrosion, indicating that it was a feasible absorbent. However, the restricted solubility of PZ in water results in problems when a solution with a high PZ concentration is loaded in cold weather. When using this mixed absorbent, it was discovered that the CO_2 collection amount and efficiency for various lean loadings were much higher than for the normal 7.0 m MEA aqueous solution [27]. As a consequence of BZ adding an amine group to the solvent, which raises the process's loading capacity, the results indicate that adding 5% of BZ to the MEA-DETA solution boosts the removal efficiency by 10% (from 82% to 92%) as shown in Fig. 11 and Fig. 12.

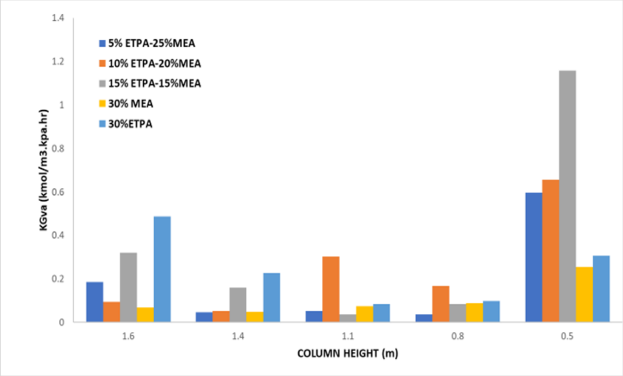


Fig. 10. Volumetric mass transfer coefficient for MEA-TEPA for each stage of packing bed at 6 LPM gas flowrate with 15 mole % CO_2, 20 ml/ min of amine with 30wt% concentration T=298K and P=1 bar

In addition to removal efficiency, there was a 0.1 km/m^3.kpa improvement in the carbon dioxide volume rate. On the other hand, if BZ% is increased by more than 5%, the number of carbon chains will rise, which will decrease the amine blends' solubility and diffusivity and slow down the absorption rate. Piperazine is widely used as a motivator to raise the absorption capacity of the blends since it contains two amine groups in its structure. Fig. 11 and Fig. 12. The results show that removal efficiency rose from 82% to 97% by adding only 5% of pz as promoters to the MEA-DETA mixture. While KGav increased from 0.1 to around 0.25 km/m^3.kpa as shown in Fig. 13 and Fig. 14.

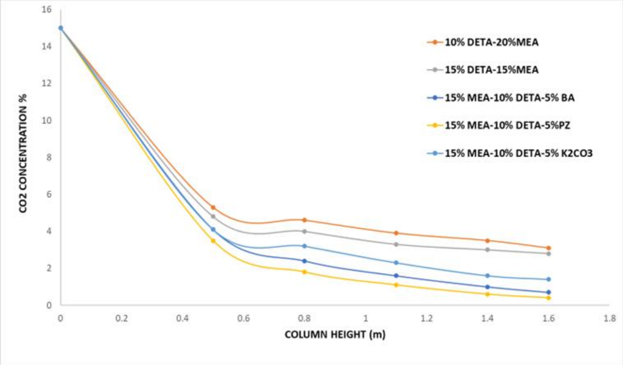


Fig. 11. Carbon dioxide concentration of MEA-DETA system with promoters along the column height at 6 LPM gas flowrate with 15 mole % CO_2, 20 ml/ min of amine with 30wt% concentration T=298K and P=1 bar

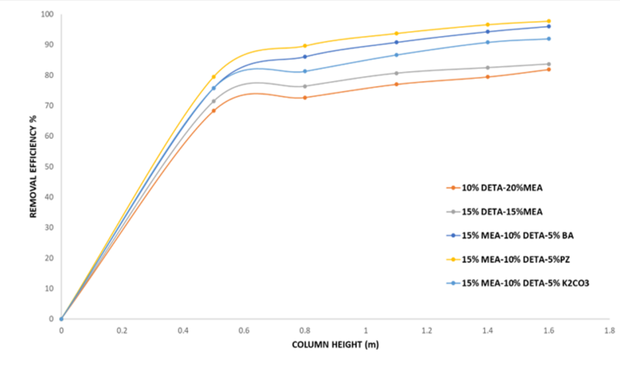


Fig. 12. Carbon dioxide removal efficiency of the MEA-DETA system with promoters along the column height at 6 LPM gas flowrate with 15 mole % CO_2, 20 ml/ min of amine with 30wt% concentration T=298K and P=1 bar

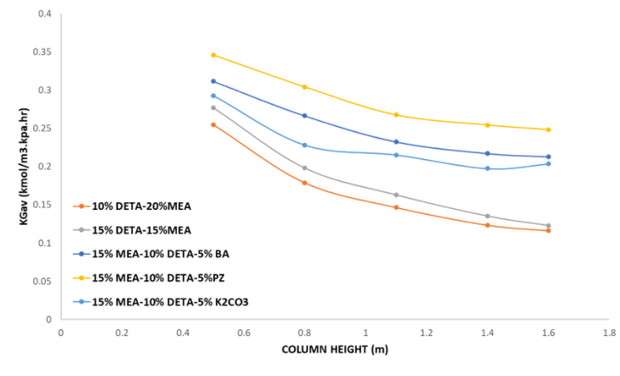


Fig. 13. Volumetric mass transfer coefficient for MEA-DETA with promoters along the column length at 6 LPM gas flow rate with 15 mole % CO_2, 20 ml/ min of amine with 30wt% concentration T=298K and P=1 bar

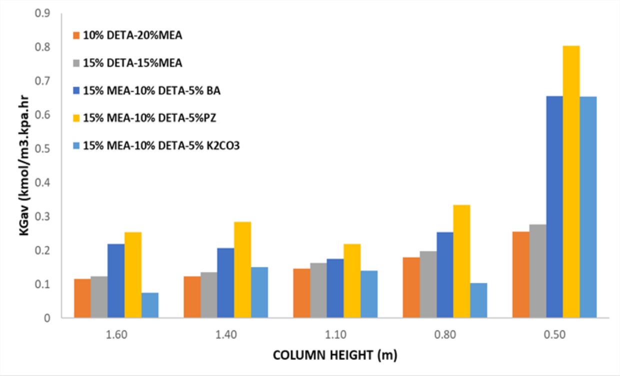


Fig. 14. Volumetric mass transfer coefficient for MEA-DETA with promoters for each stage of packing bed at 6 LPM gas flow rate with 15 mole % CO_2, 20 ml/ min of amine with 30wt% concentration T=298K and P=1 bar

b. Promoters with MEA- TEPA

Promoters such as benzylamine (BZ), PZ, and K_2CO_3 are studied by mixing them with 15% MEA and 10% TEPA to raise the carbon dioxide capacity and mass transfer rate of bending amines.

However, the results show that the removal efficiency and KGav is declined when added BZ and K_2CO_3 as promoters to the MEA-TEPA solution as shown in Fig. 15 and Fig. 16. Using PZ as promoters leads to 2% increases in the removal efficiency, while KGav values have a very minor change, as shown in Fig. 17 and Fig. 18. It was discovered that piperazine (PZ) in an aqueous solution had low volatility, a high reaction rate, and little apparatus corrosion, indicating that it was a feasible absorbent. However, the restricted solubility of PZ in water results in problems when a solution with a high PZ concentration is loaded in cold weather. When using this mixed absorbent, it was discovered that the CO_2 collection amount and efficiency for various lean loadings were much more than that of the typical 7.0 M MEA water solution [27].

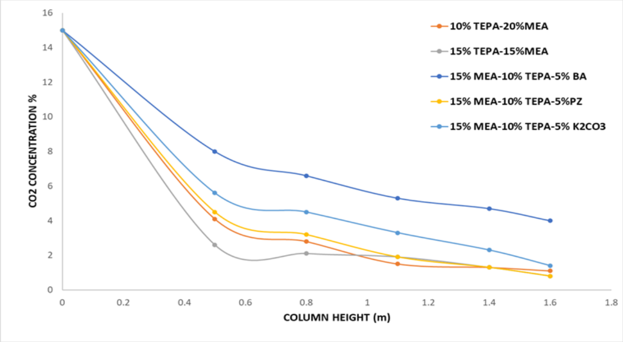


Fig. 15. Carbon dioxide concentration of MEA-TEPA system with promoters along the column height at 6 LPM gas flowrate with 15 mole % CO_2, 20 ml/ min of amine with 30wt% concentration T=298K and P=1 bar

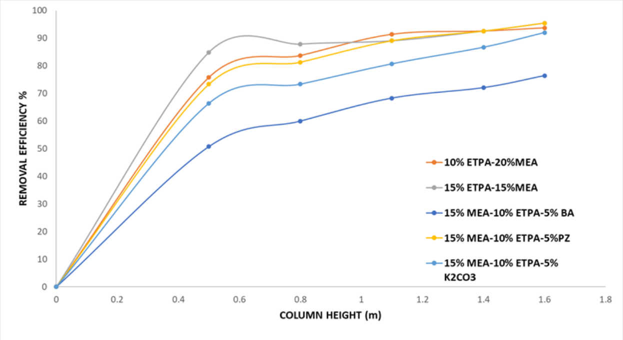


Fig. 16. Carbon dioxide removal efficiency of MEA-TEPA system with promoters along the column height. at 6 LPM gas flowrate with 15 mole % CO_2, 20 ml/ min of amine with 30wt% concentration T=298K and P=1 bar

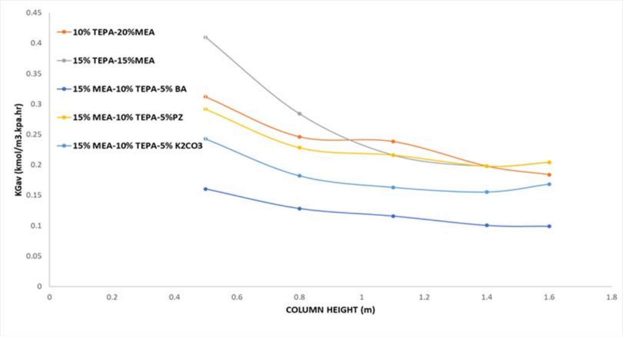


Fig. 17. Volumetric mass transfer coefficient for MEA-TEPA with promoters along the column length at 6 LPM gas flowrate with 15 mole % CO_2, 20 ml/ min of amine with 30wt% concentration T=298K and P=1 bar

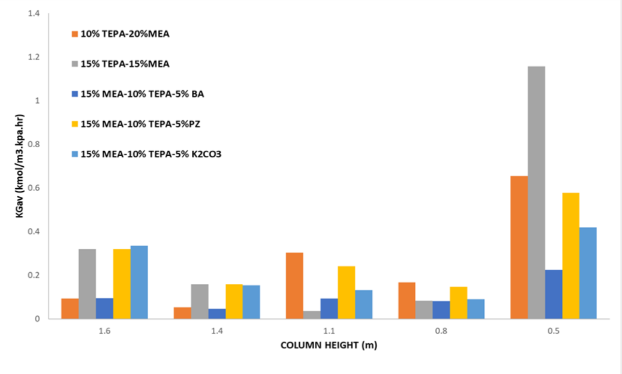


Fig. 18. Volumetric mass transfer coefficient for MEA-TEPA with promoters for each stage of packing bed at 6 LPM gas flow rate with 15 mole % CO_2, 20 ml/ min of amine with 30wt% concentration T=298K, and P=1 bar

5- Conclusion

The study concludes that combining diethylenetriamine (DETA) and tetraethylenepentamine (TEPA) with traditional monoethanolamine (MEA) significantly advances the absorption rate and CO_2 removal efficiency. The outcomes demonstrate that increasing the concentrations of DETA and TEPA enhances loading capacity, removal efficiency, and mass transfer rates for the selected blended amines. DETA, in particular, is vital for reducing capital and operational costs in CO_2 absorption processes, offering notable advantages over blends with lower DETA levels.

Diethylenetriamine, as a blending agent with a higher mass ratio, has the potential to significantly reduce the capital and operational costs of carbon dioxide absorption process equipment. It revealed higher values for KGav, cyclic capacity, and carbon dioxide absorption rate than the study's lower-mass-ratio TEPA blending. Based on these results, it makes sense to believe that diethylenetriamine (TEPA) would be an effective absorbent to enhance carbon dioxide absorption when combined with traditional MEA.

Promoters such as benzylamine, piperazine, and K_2CO_3 were also investigated when mixed with bi-amines like MEA- DETA and MEA- TEPA. The results show that piperazine has the most significant effect on removal efficiency and absorption performance.

Moreover, the utilization of three chemical promoters, benzylamine (BZ), piperazine (PZ), and potassium carbonate (K_2CO_3), was investigated in conjunction with MEA-DATA and MEA-TEPA blends. Among these, PZ demonstrated a vital, significant effect, boosting the removal efficiency to over 97% when 5% was added to the MEA-DETA mixture. Similarly, BZ improved the removal efficiency to 94% when blended with MEA-TEPA.

In contrast, removal efficiency and KGav were reduced when BZ and K_2CO_3 were used as promoters in the MEA-TEPA mixture. These findings underscore the efficacy of DETA and TEPA in improving carbon dioxide absorption and highlight the critical role of PZ as a promoter in optimizing the performance of absorption systems.

Acknowledgment

We would like to sincerely thank the Department of Chemical Engineering at the University of Baghdad's College of Engineering for all of their help and resources in making this research feasible. Their knowledge and direction were invaluable to our achievement.

Nomenclature

α	CO_2 loading of Amine
CO_2	Carbon dioxide
η	Removal efficiency of CO_2
α_{CO2}	CO_2 loading
$\alpha_{CO2.eq}$	CO_2 loading at equilibrium
C_{amine}	Concentration of amine
y_{CO2}	CO_2Concentration in the bulk gas side
C_{HCl}	HCL Concentration
$C_{active\ amine}$	active amine Concentration
DETA	Diethylenetriamine
dZ	Packing Differential height section
E	Enhancement factor
y^*_{CO2}	CO_2 equilibrium concentration
$y_{CO2,in,}$	INLET gas CO_2 concentration
HCl	Hydrochloric acid
$a_{v,}$	Interfacial area
Y_{CO2}	The molar ratio of CO_2 in the bulk gas side
MEA	Monoethanolamine
N_2	Nitrogen gas
N_{CO2}	Overall CO_2 molar flux
K_Ga_v	Overall mass transfer coefficient
Z	height of Packed bed
k_L^O	mass transfer coefficient of liquid phase
G	Total molar flow rate of inert gas
$y_{CO2,out}$	Outlet gas stream mole fraction of CO_2

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التخلص من ثاني أكسيد الكربون باستخدام مخاليط المحاليل الامينية في برج محشو بصورة عشوائية

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الخلاصة

العديد من الباحثين يقومون حالياً بالبحث في التقاط وتخزين ثنائي أكسيد الكربون نظراً إلى أن هناك توجهات لوضع حد لظاهرة الاحتباس الحراري العالمية. تعد عملية الامتصاص الكيميائي لثاني أكسيد الكربون هي أكثر الطرق فعالية. تتضمن هذه الدراسة إمكانية تطبيق واختبار أداء خليط من المحاليل الأمينية لاحادي ايثانول امين(MEA) مع ثنائي اثيلين ثلاثي امين (DETA) كخليط كيميائي ممتص. تم التحقق من الخليط في برج امتصاص محشو عشوائياً بحشوات حلقية. تقدم نتائج اداء عملية الامتصاص من حيث الثابت العام الانتقال الكتلة (K_Ga_v) وكذلك كفاءة التقاط ثاني أكسيد الكربون (η). DETA: MEA مع نسبة خلط وزنية ١:١ وتركيز وزني كلي ٣٠٪ يمكن أن تعطي أعلى K_Ga_v بقيمة $(kmol/(m^3*Kpa*hr))$٠,١٥٧٢ و كفاءة التقاط ثاني أكسيد الكربون بنسبة ٩٨,٧٩ في المائة. بينما في نفس الظروف من حيث معدل تدفق السائل والغاز، لكن بخلط DETA: MEA بنسبة خلط وزنية ٠,٢٥:١ حيث ان قيمتا K_Ga_v و η تساويان: $(kmol/(m^3*Kpa*hr))$ ٠,١١٩٨ و٩٦,٣٧ في المائة على التوالي. استناداً إلى هذه النتائج فمن المنطقي افتراض أن المحلول الاميني لثنائي اثيلين ثلاثي امين (DETA) سيكون بمثابة خليط واعد وفعال لازالة ثاني أكسيد الكربون.

الكلمات الدالة: الامتصاص الكيميائي، ازالة ثاني اكسيد الكربون، البرج المحشو، خليط الكانول أمين، احادي ايثانول امين، ثنائي اثيلين ثلاثي امين.