Investigation of overall mass transfer coefficient of CO$_2$ absorption in to aqueous blended Monoethanolamine (MEA), Diethanolamine (DEA) and Triethanolamine (TEA) measured in Bubble column Reactor solution

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Abstract: Mixtures of different types of amine solution (primary Monoethanolamine (MEA)), secondary: diethanolamine (DEA) and tertiary: triethanolamine (TEA) were experimentally used to investigate the overall mass transfer coefficient ($K_{ga}$) at different operating parameters. The experiments were made in a bubble column reactor (BCR) with 1.5 m in high and 0.1 m inside diameter as a gas-liquid contactor at 25°C and atmospheric pressure, using a simulation gaseous mixture (air, carbon dioxide) with recycle stream (circulation process). For efficient experimentation, the Taguchi method was applied for experimental design. A four factor and three levels was chosen for this study and it was exploded using L9 ($3^4$) orthogonal array design. These parameters for circulation process were namely: gas flow rate 10, 15, and 20 L/min, air flow rate 100, 150, and 200 L/h, liquid flow rate 5, 10, and 15 L/min and time absorption time 30, 60, and 90 min. To understand the effectiveness order of different operating parameters, two factors namely, overall mass transfer coefficient ($K_{ga}$), and CO$_2$ loading (a) are to be exploded. A Shimadzu GC-8A Gas Chromatograph with thermal conductivity detector was used to measure the CO$_2$ concentration absorbed in aqueous blended solution. As per Taguchi analysis the significance sequence influencing the parameter and optimum condition can be determined. The maximum value for CO$_2$ loading was 3.439 (mol CO$_2$/mol amine) at 20 L/min gas flow and 15 L/min liquid flow and 200 L/h air flow for 60 min from absorption time. The performance was evaluated in terms of the overall mass transfer coefficient, $K_{gas}$, the results show that max value of $K_{gas}$ was 0.08 S$^{-1}$.

Keywords: CO$_2$ Absorption, Monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), overall mass transfer coefficient ($K_{ga}$), bubble column reactor (BCR), Taguchi method

1. Introduction

Currently, increasing in the carbon dioxide emission in to the atmosphere have already triggered a series of undesirable consequence such as such as global warming and climate change, which are considered to have close relationships with several environmental issues including rising sea levels, and glacier smelting, etc.[1][2]. Globally, CO$_2$ emitted from power plants is around 40% of the total CO$_2$ emissions and under business as usual mode
it is expected to increase up to 60% by the end of this century [3]. So, carbon dioxide separation technology is enjoying an increasingly larger market because of the urgent demand to respond to both global warming and energy consumption. Meanwhile the most widely applied and effective methods for CO$_2$ capture is chemical absorption using novel absorbents that possess more efficient capture performance and are more energy-saving such as mixed amine solution [4]. In previous study blended alkanolamine solvents, primary: monoethanolamine (MEA), secondary: diethanolamine (DEA) and tertiary: triethanolamine (TEA) were used for this investigation. MEA is one of the predominant solvents due to its advantages such as, relatively low material cost, high boiling point capability, low viscosity, reusability, fast absorption rate and rich experience in industrial applications, complete solubility in water, and solubility with other amines [5][6] showed that the overall mass transfer coefficient (K$_G$) for aqueous MEA was at least 1.5–2 times higher than for ammonia. This result is driven due to both the lower temperature and the lower reactivity of ammonia towards CO$_2$. However, there are limitations of using MEA solution alone, i.e. degradation in the presence of O$_2$, Sox and NOx, high energy consumption for solvent regeneration and corrosive. To mitigate such limitations MEA is blended with other solvents like diethanolamine (DEA) and triethanolamine (TEA). Diethanolamine (DEA) is the most important secondary amine employed both in laboratory and in industry, and therefore, DEA is generally included in the mixtures that involve secondary alkanolamines. Triethanolamine (TEA) is less applied both in research and industry. Due to the slower reaction with carbon dioxide, actually tertiary amines are not regarded an effective alternative to the most widely used primary and secondary ones, i.e., monoethanolamine (MEA) or diethanolamine (DEA), but their use in amine blends becomes more and more frequent. Furthermore, the addition of tertiary amines with primary and secondary amines presents certain advantages compared to other alkanolamines used as absorbents despite the slower reaction with carbon dioxide. Industrially relevant problems such as cost, energy consumption for absorbent regeneration, corrosion of industrial equipment materials, foam production, losses of solvent by evaporation, increase the CO$_2$ absorption capacity, and solvent degradation in the presence of oxygen are reduced by using tertiary amines. There are also another tertiary amine have been used by some researchers was N-methyl diethanolamine (MDEA). The slower absorption rate of tertiary amines could be explained by their reaction with carbon dioxide the tertiary amines do not react directly with CO$_2$ to form stable carbamates, despite this behavior reduces the solvents’ regeneration costs. Also, TEA is used in more complex systems to improve the CO$_2$ loading. More specifically this substance (TEA) has been employed for CO$_2$ absorption in the presence of solids, with polymers aqueous solutions or using non-aqueous systems to carry out the capture reaction between CO$_2$ and TEA. Other studied about the use of this kind of aqueous solutions for CO$_2$ capture is the work developed by [7] that employ TEA aqueous solutions in a hybrid membrane contactor by means of chemical reaction in one chamber of the contactor. The results show significantly improvements for CO$_2$ capture regards packed columns working at room temperature.

A bubble column reactor (BCR) with the liquid phase operating in recycle mode was used in this paper. Due to noncomplex design of this bubble column, low investment and current cost, high gas–liquid interfacial area and high absorption performance[8]. This research used MEA as the basic solvent, which was combined with the two kinds of potential amines (DEA and TEA) to screen the best combination of blended amine with suitable conditions. This Study was focused on the improvement of amine solvents in order to reach a high CO$_2$ capture performance and a low cost of operation, also to determine the overall mass transfer coefficients ($k_{Gav}$) performance of the CO$_2$ absorption process.
2. Determination Overall mass Transfer Coefficient

Mass transfer coefficient is an important part of this research. Mass transfer occurs when a component, A, in a gas phase transfers across a gas-liquid interface into a liquid phase. Component A transfers from the gas phase into the liquid phase because of the concentration gradient in the direction of mass transfer within each phase. Several correlations have been used to predict mass transfer coefficients in chemical engineering processes. [9] predicted correlations for overall mass transfer coefficients of bubble column reactor as in equation below. The final equation that determines the overall mass transfer coefficient, $K_{Ga}$, can be calculated using Equation (1)

$$K_{Ga} \ (s^{-1}) = \frac{Q_g^{(L)}}{V_L (L)} \ ln \frac{F_1 \ mol}{F_2 \ mol}$$

Where :

$Q_g^{(L)}$=Gas flow rate, ($\frac{L}{s}$)

$F_1$=Molar flow rate of CO$_2$ at inlet, ($\frac{mol}{s}$)

$F_2$=Molar flow rate of CO$_2$ at outlet, ($\frac{mol}{s}$)

$V_L$=is the volume of liquid in the absorber.

3. Experimental Design

The Taguchi method was used as an experimental design, in order to reduce the large amount of experiments. The first step was the selection of independent variables. In this study the process parameters used in here are four parameters for circulation, namely: gas flow rate, air flow rate, liquid flow rate and time of absorption. Each factor has three levels as shown in Tables (1). Using the Taguchi experimental design, the orthogonal array L9($3^4$) showed nine experiments, thereby reducing the number of experiments needed and the research cost by over 80%. Table (2) presents the combination of experiments in the orthogonal array for circulation process.

### Table (1). Factors and levels used in this study.

| Factors                  | 1   | 2   | 3   |
|--------------------------|-----|-----|-----|
| Gas flow rate (L/min)    | 10  | 15  | 20  |
| Air flow rate (L/h)      | 100 | 150 | 200 |
| Liquid flow rate (L/min) | 5   | 10  | 15  |
| Absorption Time (min)    | 30  | 60  | 90  |
**Table (2)** Orthogonal arrays for experimental design for circulation process

| Experiment No. | A (gas flow) L/min⁻¹ | B (air flow) L/h⁻¹ | C (Liquid flow) L/min⁻¹ | D (Time) Min |
|----------------|----------------------|--------------------|-------------------------|--------------|
| 1              | 10                   | 100                | 5                       | 30           |
| 2              | 10                   | 150                | 5                       | 60           |
| 3              | 10                   | 200                | 5                       | 90           |
| 4              | 15                   | 100                | 10                      | 60           |
| 5              | 15                   | 150                | 10                      | 90           |
| 6              | 15                   | 200                | 10                      | 30           |
| 7              | 20                   | 100                | 15                      | 90           |
| 8              | 20                   | 150                | 15                      | 30           |
| 9              | 20                   | 200                | 15                      | 60           |

**4. Experimental Procedure**

The chemical solvent employed that used are shown in table 3

**Table (3) Chemical materials (Amines) used in this work**

| Chemical Name          | Abbreviation | Chemical formula | Molecular weight [g/mol] | Density g/cm³ |
|------------------------|--------------|------------------|--------------------------|---------------|
| Monoethanolamine       | MEA          | C₃H₇NO           | 61.084                   | 1.0117        |
| Diethanolamine         | DEA          | C₄H₁₀NO₂         | 105.137                  | 1.097         |
| Triethanolamine        | TEA          | C₆H₁₅NO₃        | 149.190                  | 1.124         |

Aqueous solutions were prepared with de-ionized water. The amine concentration in the mixtures was 10% volume percent for MEA, 5% volume percent for DEA, and 5% volume percent for the first experiments and 10% for the other from TEA. All the experiments were performed at atmospheric pressure and at temperature equal to 298.15 K. The experimental set-up apparatus used for carbon dioxide absorption is shows in Figure 1.
A bubble column reactor (BCR) with the liquid phase operating in recycle mode was used to carry out this experimental. The reactor is made of Perspex with inner diameter (0.1) m and the total high of the column was (1.5) m.

Before introducing the solution of blended amine into bubble column reactor, pure $CO_2$ and pure air from (compressor) were mixed where the air flow rate was regulated to an appropriate value in the range 100-200 L/h var. The gas flow rate was used to maintain a certain flow rate during the injection of carbon dioxide, the flow rate of the feed gas ($CO_2$) supplied from gas cylinder was adjusted and controlled by ($CO_2$) gas flow rate in the range 10-20 L/min, and then it was fed through the down of the bubble column. The gas inlet was a bubbler type and an perforated plate used in bubble column is constructed from aluminum of (2 mm) thickness with perforated holes of 2 mm diameter on a triangular pitch of 11 mm. The total holes were 79 holes was used to increase the contact area between the liquid phase and carbon dioxide gas phase. The pressure gauges were used to indicate the inlet and outlet pressures of the gas and liquid.

In order to remove impurities in the reactor before and after every experiment, de-ionized water was used for ten minutes. All amine solutions were prepared using de-ionized water and volumetric glass ware, an aqueous solution was prepared using 1L of water for each experiment. The prepared absorbent liquid (solvent) was introduced at the upper section of absorption column with the help of a liquid flow rate which was regulated to an appropriate via 5,10,15 L/min, and a needle valve was installed on the top of the column to control the liquid flow rate so as to create counter current contact between gas and liquid, the exit liquid at the bottom was recycled using a Shimge centrifugal pump. The bubble column reactor was filled with the liquid solution to a level of 100 cm above the distributer and re-circulate. The exiting liquid was sampled and was taken from the bubble column reactor every 15 second in a 10 ml flask bottle. After several samples taken, the procedure of analysis was applied.
5. Results and discussion

In this work high performance a Shimadzu GC-8A Gas Chromatograph was used for analysis the samples that were obtained in experimental work in the laboratory of scientific studies and research in the region of Algiers - Al-Diwaniya (Iraq)

The absorption loading of $CO_2$ of (MEA + DEA + TEA) which is in the range of (1.146–3.439) moles of $CO_2$ absorbed per mole of amine. $CO_2$ loading was calculated by integrating differences between the concentrations of injected $CO_2$ and the concentrations of emitted $CO_2$. All the absorbents used in the experiments reached equilibrium at an appropriate time, when completion of the reactions between $CO_2$ and the absorbents. The amount of the $CO_2$ before being injected into the reactor and the amount of the $CO_2$ emitted after reactions were calculated by applying the ideal gas equation. The overall mole of $CO_2$ absorbed in the absorbent can be calculated by subtract mol of $CO_2$ inlet from mol of $CO_2$ outlet as in Equation (2), and the $CO_2$ loading can be calculated through Equation (3). $CO_2$ loading is defined as mole of $CO_2$ absorbed per mole of amine.

$$n_{CO_2, abs} = n_{CO_2, IN} - n_{CO_2, out} \quad (2)$$

$$\alpha = \frac{\text{mol of } CO_2}{\text{mol of amine}} \quad (3)$$

Table (4) The results of $CO_2$ loading of the experiments for circulation process by using (MEA=10%, DEA=5%, and TEA=5%) as blended solution

| Exp. No. | Sample | Gas flow $L/min^{-1}$ | Air flow $L/h^{-1}$ | Liquid flow $L/min^{-1}$ | Absorption time/min | $CO_2$ loading (mol $CO_2$/mol amine) | Absorption Capacity |
|----------|--------|-----------------------|---------------------|--------------------------|---------------------|--------------------------------------|------------------|
| Group A/30 min |
| 1 | Sample1 | 10 | 100 | 5 | 15 | 1.146 | 0.265 |
| 2 | Sample2 | 10 | 100 | 5 | 30 | 1.711 | 0.397 |
| Group B/60 min |
| 1 | Sample1 | 10 | 150 | 5 | 15 | 1.230 | 0.281 |
| 2 | Sample2 | 10 | 150 | 5 | 30 | 1.987 | 0.454 |
| 3 | Sample3 | 10 | 150 | 5 | 60 | 2.425 | 0.550 |
| Group C/90 min |
| 1 | Sample1 | 10 | 200 | 5 | 15 | 1.408 | 0.324 |
| 2 | Sample2 | 10 | 200 | 5 | 30 | 1.721 | 0.399 |
| 3 | Sample3 | 10 | 200 | 5 | 60 | 2.893 | 0.661 |
| 4 | Sample4 | 10 | 200 | 5 | 90 | 3.030 | 0.687 |
| Group D/60 min |
| 1 | Sample1 | 15 | 100 | 10 | 15 | 1.402 | 0.323 |
| 2 | Sample2 | 15 | 100 | 10 | 30 | 2.395 | 0.548 |
| 3 | Sample3 | 15 | 100 | 10 | 60 | 3.001 | 0.683 |
Table (5) The results of CO₂ loading of the experiments for circulation process by using (MEA=10%, DEA=5%, and TEA=10%) as blended solution

| Exp. No | Sample | Gas flow L/min⁻¹ | Air flow L/h⁻¹ | Liquid flow L/min⁻¹ | Absorption time/min | CO₂ loading (mol CO₂/mol amine) | Absorption Capacity |
|---------|--------|-----------------|----------------|---------------------|---------------------|----------------------------------|---------------------|
| 1       | Sample 1 | 15              | 150            | 10                  | 15                  | 1.365                            | 0.318               |
| 2       | Sample 2 | 15              | 150            | 10                  | 30                  | 2.159                            | 0.494               |
| 3       | Sample 3 | 15              | 150            | 10                  | 60                  | 2.837                            | 0.645               |
| 4       | Sample 4 | 15              | 150            | 10                  | 90                  | 2.951                            | 0.667               |

Group E/90 min

| Exp. No | Sample | Gas flow L/min⁻¹ | Air flow L/h⁻¹ | Liquid flow L/min⁻¹ | Absorption time/min | CO₂ loading (mol CO₂/mol amine) | Absorption Capacity |
|---------|--------|-----------------|----------------|---------------------|---------------------|----------------------------------|---------------------|
| 1       | Sample 1 | 15              | 200            | 10                  | 15                  | 2.087                            | 0.476               |
| 2       | Sample 2 | 15              | 200            | 10                  | 30                  | 2.560                            | 0.574               |

Group F/30 min

| Exp. No | Sample | Gas flow L/min⁻¹ | Air flow L/h⁻¹ | Liquid flow L/min⁻¹ | Absorption time/min | CO₂ loading (mol CO₂/mol amine) | Absorption Capacity |
|---------|--------|-----------------|----------------|---------------------|---------------------|----------------------------------|---------------------|
| 1       | Sample 1 | 20              | 100            | 15                  | 15                  | 1.692                            | 0.385               |
| 2       | Sample 2 | 20              | 100            | 15                  | 30                  | 2.675                            | 0.607               |
| 3       | Sample 3 | 20              | 100            | 15                  | 60                  | 3.168                            | 0.720               |
| 4       | Sample 4 | 20              | 100            | 15                  | 90                  | 3.302                            | 0.748               |

Group G/90 min

| Exp. No | Sample | Gas flow L/min⁻¹ | Air flow L/h⁻¹ | Liquid flow L/min⁻¹ | Absorption time/min | CO₂ loading (mol CO₂/mol amine) | Absorption Capacity |
|---------|--------|-----------------|----------------|---------------------|---------------------|----------------------------------|---------------------|
| 1       | Sample 1 | 20              | 150            | 15                  | 15                  | 1.900                            | 0.436               |
| 2       | Sample 2 | 20              | 150            | 15                  | 30                  | 2.773                            | 0.628               |

Group H/30 min

| Exp. No | Sample | Gas flow L/min⁻¹ | Air flow L/h⁻¹ | Liquid flow L/min⁻¹ | Absorption time/min | CO₂ loading (mol CO₂/mol amine) | Absorption Capacity |
|---------|--------|-----------------|----------------|---------------------|---------------------|----------------------------------|---------------------|
| 1       | Sample 1 | 20              | 200            | 15                  | 15                  | 2.526                            | 0.578               |
| 2       | Sample 2 | 20              | 200            | 15                  | 30                  | 3.110                            | 0.703               |
| 3       | Sample 3 | 20              | 200            | 15                  | 60                  | 3.439                            | 0.777               |

When comparison of the results obtained for CO₂ loading capacity Vs. reaction time for the tested aqueous amine solution for groups (A, B, C, D) and (E, F, G, H, I) as shown in Figures. 2 and 3 respectively. We found that an increase in the CO₂ loading of an absorbent with increasing time and mean that the solubility of carbon dioxide is increased under various parameters condition.

![Fig.2 Maximum CO₂ absorption capacity Vs. absorption time for (10MEA+5%DEA+5% TEA)](image-url)
6. The effect of carbon dioxide loading capacity on overall mass transfer coefficient, $K_{Ga}$

The following figures shows the main effect of $CO_2$ loading on overall mass transfer coefficient $K_{Ga}$ in each group. According to equation (1) calculate the overall mass transfer coefficient $K_{Ga}$ $5^{-1}$ for circulation process. In Figures (4), and (5) it is obvious that an increase of $CO_2$ loading in amine solutions leads to a decrease in the existing active amine concentration, which consequently decreases the overall mass transfer coefficient. This effect is mainly attributed to the amount of $CO_2$ loading in the amine solution is high. Where (MEA+DEA+TEA) blended amine solution are used in all three figures, the mass transfer driving force from the gas phase to the liquid phase will decrease. This effect is consistent with the work of each of the researchers. (Fu, et al., 2013) [10] have investigated the $K_{Ga}$ parameter using a DETA solution, they performed the experiment on packed a absorber. They compared the $K_{Ga}$ values between DETA +– $CO_2$ and MEA – $CO_2$ systems, and found that the $K_{Ga}$ values of DETA were higher compared with MEA. In addition, they showed that by increasing the DETA flow rate, concentration, and inlet temperature, the $K_{Ga}$ values increased. Nevertheless, the $K_{Ga}$ values decreased as the $CO_2$ loading of DETA increased.

![Graph showing maximum CO2 absorption capacity Vs. absorption time for (10MEA+5%DEA+10%TEA)](image)

Fig .3 Maximum $CO_2$ absorption capacity Vs. absorption time for (10MEA+5%DEA+10%TEA)

![Graph showing progression of overall mass transfer coefficient in a function of CO2 loading for circulation processes (10% MEA+5%DEA+5%TEA)](image)

Fig (4) Progression of overall mass transfer coefficient in a function of $CO_2$ loading for circulation processes (10% MEA+5%DEA+5%TEA)
The maximum value obtained from these experiments was 0.08 $S^{-1}$ in group I at gas flow 20 L/min and liquid flow rate 15 L/min and air flow rate 200 L/h. While (Chen et al.,2015) [5] they were found that $K_{Ga}$ was 0.0342 $S^{-1}$ when absorption CO$_2$ using MEA solution. (Chen et al.,2018) absorption of CO$_2$ using aqueous ammonia solution $K_{Ga}$ was 0.051 $S^{-1}$.

7. Conclusion
The overall mass transfer coefficient ($K_{Ga}$) of carbon dioxide absorption into blended MEA-DEA-TEA solutions was experimentally measured using a laboratory-scale bubble column. The parameter used in this study were gas flow, liquid flow, air flow, and time. This study showed that the increasing by the gas flow rate, the liquid flow rate, and absorption time, the $K_{Ga}$ values increased. Also, Increasing the CO$_2$ loading of amines lead to a $K_{Ga}$ decrease.

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