

Article

Experimental Evaluation of Chemical Reactions Involved in Ultrasonic-Assisted Absorption of Bulk CO₂

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Abstract: As the most mature natural gas sweetening process, absorption has always been improved to meet the separation requirement. Recently, ultrasonic irradiation has been proposed as a technique that can intensify CO₂ absorption. However, further studies are still required, particularly focusing on the sonochemical effect. Since the influence of the sonochemical effect on the reaction pathway is still debatable, attention must be given to verifying the influence of ultrasonic irradiation on the chemical reactions of CO₂ absorption. Hence, this work aims to evaluate the influence of OH radicals generated by the sonochemical effect on the chemical reactions involved during CO₂ absorption using promoter-free methyldiethanolamine (MDEA). For the evaluation, various samples under irradiated and non-irradiated conditions are analyzed using the HPLC characterization technique. The results show that the hypothesis of changing the reaction pathway due to the presence of the sonochemical effect is invalid. However, it can accelerate the generation of hydroxyl radicals (OH) via water sonolysis. Thus, the origin of sonochemistry in aqueous solutions is defined as water sonolysis. The analysis of the CO₂ absorption rate also demonstrates the presence of accelerated chemical reactions (contributed by the OH radicals), which could potentially make the slow kinetic MDEA more practical for industrial application.



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Keywords: absorption; ultrasonic irradiation; sonochemical effect; HPLC characterization; reaction pathway

1. Introduction

The demand for natural gas is predicted to rise by more than 60% between now and 2040. Depending on the geological condition of the reservoir, the raw natural gas has a wide range of gases, including methane, heavier hydrocarbons such as ethane, propane, isobutene, normal butane, and a substantial amount of impurities such as CO₂, H₂S, and CO [1]. Removing acidic impurities from natural gas, especially CO₂, is a vital step toward further utilization of this energy source. Such CO₂ elimination in both on/offshore natural gas wells can be achieved by developing carbon capture and storage processes that permit the mitigation and utilization of CO₂.

Currently, absorption, especially chemical absorption, is the most developed separation process widely used to capture CO₂ from raw natural gas [2]. Nevertheless, this process still suffers from various drawbacks, including high energy consumption for solvent regeneration, solvent loss, equipment corrosion, and large column sizes [3,4]. These disadvantages pose various technical and financial challenges to the CO₂ absorption process, necessitating the search for intensification techniques. Such process intensification techniques can reduce the size of conventional absorption columns, decrease the equipment capital cost, and make CO₂ absorption more feasible. Available techniques to intensify the mass transfer of the absorption process include packed bed columns (PB), rotating

packed bed columns (RPB), hollow fiber membrane contactors (HFMC), bubble columns (BC), microchannel reactors (MC), and ultrasonic irradiation [5,6]. Among them, ultrasonic irradiation is a novel technique requiring extensive investigations before industrial scaleup.

In general, ultrasonic irradiation is expressed as sound waves with frequencies higher than the upper limit of human hearing ability, ranging from 20 kHz to 500 MHz. Depending on the applied frequency and the presence of the sonophysical and sonochemical effects, this technique has the potential to be used in different research areas, including food technology [7], cleaning [8], medical treatment [9], crude oil upgrading [10], synthesis of nanomaterials [11,12], and enhancement of multiphase reactions [13,14]. However, using high-frequency ultrasonic irradiation in the natural gas purification field is limited, particularly as a potential intensification technique for CO₂ absorption. The concept of using ultrasonic irradiation in the CO₂ absorption process was first proved by Tay et al. (2017) [15–17]. They investigated the effect of high-frequency ultrasonic irradiation on the CO₂ absorption performance of a batch lab-scale reactor. Three different solvents were tested, including water, monoethanolamine (MEA), and potassium carbonate (K₂CO₃). The results showed a remarkable rise in the CO₂ absorption rate by utilizing ultrasonic irradiation with a frequency of 1.7 MHz. They stated that ultrasonic irradiation can improve CO₂ absorption performance because of the sonochemical and sonophysical effects. However, particular attention was given to the sonophysical effects. After proving the concept, the focus switched to the continuous mode. Hence, Yusof et al. (2019) developed a novel continuous high-frequency ultrasonic contactor system for the CO₂ absorption process [18]. They investigated the effect of different operating parameters on the ultrasonic-assisted CO₂ absorption from natural gas using water. They mentioned that the continuous ultrasonic contactor system for CO₂ absorption performed better than other contactors. According to their results, the continuous ultrasonic contactor system showed the highest mass transfer coefficient (0.037 s^{−1}) between the other contactors, including the bubble column, stirred vessel, and counter-current packed column. They did not, however, address the significance of sonophysical and sonochemical effects on such improvements [18]. To suit the industrial mode, they also evaluated the performance of the proposed continuous system with MEA. The influence of various operating parameters on the overall mass transfer coefficient was evaluated. They reported that at the optimized conditions for the CO₂-MEA system, the high-frequency ultrasonic absorption system could intensify the mass transfer up to 12 times compared to the conventional packed bed column. They concluded that the sonophysical effects are mainly responsible for the enhanced CO₂ absorption process in the continuous high-frequency ultrasonic reactor [19]. The effects of different absorbents, including diethanolamine (DEA), sodium hydroxide (NaOH), and sodium carbonate (Na₂CO₃), on ultrasound-assisted CO₂ absorption were investigated in the study conducted by Marjanian et al. (2021) [20]. They stated that the extent of improving CO₂ absorption performance in the ultrasonic-assisted absorption system depends on the absorbent type.

As a way forward to maturing this technique, more fundamental research on CO₂ absorption performance utilizing other commercial chemical absorbents and focusing on sonochemical effects was required. Therefore, in our previous research [21], attention was given to MDEA as a chemical absorbent with a high inherent CO₂ absorption capacity but slow absorption kinetics with CO₂. The influence of different operating parameters on CO₂ absorption performance in an ultrasonic-assisted batch reactor was evaluated using MDEA in single and blended forms. The potential of the ultrasonic-assisted reactor was then further elucidated through a comparative analysis with magnetic stirring and non-irradiated conditions. The findings demonstrated that the CO₂ absorption rate in the ultrasonic-assisted reactor was approximately 28 and 52 times higher than in the stirred reactor and the non-irradiated condition, respectively, when 50% promoted-free MDEA was utilized. Even with the addition of 5% piperazine (PZ), the ultrasonic-assisted CO₂ absorption system outperformed other systems. Compared to the magnetic stirred reactor, the CO₂ absorption rate in this case was 17 times higher. Furthermore, compared to the

non-irradiated condition, the CO₂ absorption rate was 54 times higher. Both sonochemical and sonophysical effects were responsible for the increase in the CO₂ absorption rate [21]. However, as the role of the sonochemical effect on the improvement of the CO₂ absorption process in the ultrasonic-assisted reactor was not yet elucidated, our recent study aimed to parametrically quantify the sonochemical effect during CO₂ absorption in the ultrasonic-assisted reactor using promoter-free MDEA. A novel indirect method was implemented to identify OH radicals as the representative of the sonochemical effect. Terephthalic acid (TA) was selected as a chemical probe for detecting and scavenging OH radicals during the CO₂ absorption using promoter-free MDEA. Subsequently, the quantification was performed via scavenging of OH radicals using TA. Despite the parametric quantification, the role of the sonochemical effect on the chemical reactions involved in CO₂ absorption has not yet been investigated.

2. Theory

In general, the CO₂ absorption process contains three key steps, including vapor-liquid mass transfer, liquid-liquid mass transfer, and liquid chemical reaction [22]. By applying high-frequency ultrasonic irradiation, all these steps can be influenced due to the presence of sonophysical and sonochemical effects. Figure 1 illustrates the sonophysical and sonochemical effects induced by high-frequency ultrasonic irradiation during the CO₂ absorption process.

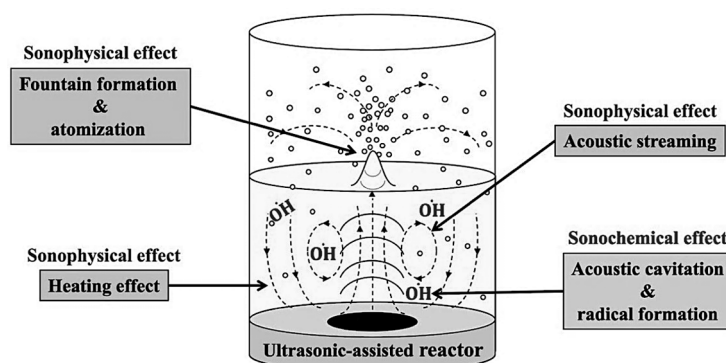


Figure 1. Different effects induced by high-frequency ultrasonic irradiation.

According to Figure 1, atomization, acoustic streaming, liquid fountain formation, and heating are the main sonophysical effects induced by high-frequency ultrasonic irradiation during the CO₂ absorption process. The sonophysical effects can improve mass transfer by adequately mixing, lowering mass transfer resistance in the liquid phase, and increasing the effective interfacial areas between the gas and liquid phases [15,16]. In contrast, the sonochemical effect is caused by a phenomenon known as acoustic cavitation [19]. Cavitation involves various steps. The three main steps of cavitation are formation (nucleation), bubble growth (expansion) during the cycles until reaching a critical size, and violent collapse in the liquid bulk. These steps are repeated consistently. In the formation step, if the ultrasonic intensity is high enough to surpass the liquid's tensile strength, there comes a point at which intermolecular forces can no longer hold the molecular structure together. Cavitation nuclei form in the liquid phase as a result of this point [23,24]. The formed microbubbles may grow rapidly if the ultrasonic intensity is sufficiently strong. This step is recognized as an expansion [25]. The implosion step happens when the cavitation bubble becomes so dense that it cannot continue absorbing energy to sustain itself. As a result, the surrounding liquid rushes into it, causing an implosion [23,26]. Each bubble functions as a core when implosion occurs, producing energy that increases the temperatures and pressure on a microscale. Due to inducing extremely high local temperature and pressure, the collapsing bubbles can create an unusual environment for chemical reactions by forming highly reactive radical species [23,27].

According to the hotspot theory, a chemical reaction happening in an ultrasonic-assisted system is a heterogeneous reaction in which reactive species are generated from the cavitation bubble. In this theory, three regions are anticipated for the incidence of chemical reactions, including (1) a hot gaseous nucleus or thermolytic zone, (2) an interfacial area having a radial temperature gradient and a local radical density, and (3) the solution bulk at ambient temperature. These three regions are shown in Figure 2.

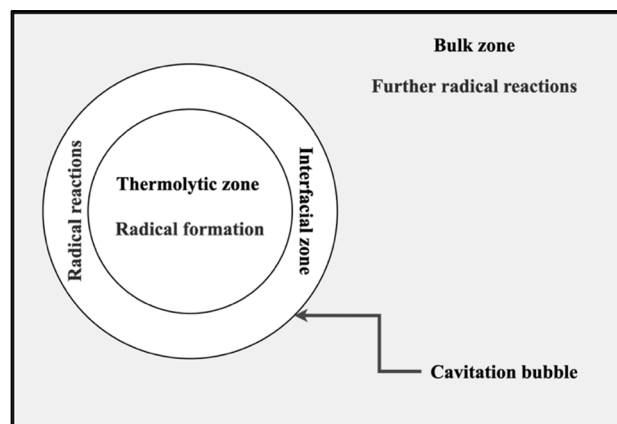


Figure 2. Reaction zones according to hotspot theory.

In the first region, which is a hot gaseous nucleus, the extreme conditions created by collapse trigger bond breakage of the presented vapors and gases within the bubble nucleus, leading to the generation of free radicals, particularly OH radicals. The formed OH radicals can either react with each other to form new molecules and radicals or diffuse into the liquid bulk [24]. The second region is the liquid shell around the imploding cavity, which is estimated to heat up to approximately 2000 K during implosion. Combustion and radical reactions (including OH generated from H₂O decomposition) occur in this solvent layer around the hot bubble. In the liquid bulk, as the last region, there is no direct sonochemical activity, but subsequent reactions with ultrasonically produced intermediates may occur. Furthermore, a limited number of radicals generated in the cavities or at the interface may move into the bulk liquid phase and react with the substrate to form new products [24,28]. Hence, there might be some differences in the reaction pathways in the ultrasonic-assisted system compared to the conventional system. Due to the generation of OH radicals, there is a hypothesis that the sonochemical effect is capable of speeding up or changing the reaction pathway of the CO₂ absorption process in the high-frequency ultrasonic-assisted system. The generated OH radicals could be the cause of the ultrasonic-assisted system's improved performance, as summarized in Table 1. However, the role of the sonochemical effect on the chemical reaction of CO₂ absorption has not been discussed. Thus, further studies are substantial to investigate the role of the sonochemical effect on the reaction pathway during ultrasonic-assisted CO₂ absorption.

Table 1. Absorption rate comparison of the various MDEA-based CO₂ absorption techniques.

Absorbent	MDEA	MDEA	MDEA	MDEA	MDEA	MDEA	
Promoter	MEA	DEA	DEA	PZ	PZ	-	
Target Gas	CO ₂	CO ₂	CO ₂	CO ₂	CO ₂	CO ₂	
Technique	WWC	WWC	WWC	DC	HFUA	HFUA	
Operating conditions	C _{MDEA}	1.5 kmol·m ⁻³	1.5 kmol·m ⁻³	1.5 kmol·m ⁻³	2.636 kmol·m ⁻³	50 wt%	50 wt%
	C _{Promoter}	0.1 kmol·m ⁻³	0.1 kmol·m ⁻³	0.4 kmol·m ⁻³	0.364 kmol·m ⁻³	5 wt%	0 wt%
	T	40 °C	40 °C	40 °C	60 °C	70 °C	70 °C
	P	0.239 bar	0.335 bar	0.4 bar	0.8 bar	11 bar	11 bar
Absorption rate		0.12 mol·h ⁻¹	0.15 mol·h ⁻¹	0.25 mol·h ⁻¹	0.12 mol·h ⁻¹	15.23 mol·h ⁻¹	4.20 mol·h ⁻¹
Reference		[29]	[30]		[31]	[21]	

3. Methodology

3.1. Materials

The materials used in this work and the specifications provided by their suppliers are presented in Table 2.

Table 2. The used materials and their respective information.

Material	Formula	Supplier	Purity	Application
Carbon dioxide	CO ₂	Air Products, Kuala Lumpur, Malaysia	99.99%	Target absorbing gas
Distilled water	H ₂ O	-	100%	Preparation of aqueous solutions
Methyldiethanolamine	C ₅ H ₁₃ NO ₂	Revlogi Materials, Puchong, Malaysia	≥99%	Main chemical absorbent
Terephthalic acid	C ₈ H ₆ O ₄	Sigma Aldrich, Burlington, MA, USA	≥99%	OH radical scavenger
Sodium hydroxide	NaOH	Sigma Aldrich, Burlington, MA, USA	≥99%	HPLC mobile phase
Disodium hydrogen phosphate anhydrous	Na ₂ HPO ₄	Merck, Darmstadt, Germany	≥99%	HPLC mobile phase

3.2. Experimental Setup

The schematic of the ultrasonic-assisted CO₂ absorption system is shown in Figure 3. The reactor was fabricated using stainless steel, operating in the batch absorption configuration. The reactor consisted of a top cover and a cylindrical body. The volume of the reactor, inner diameter, and height were 250 mL, 5 cm, and 17.8, respectively. The temperature sensor, pressure sensor, gas inlet and outlet, and pH probe were on the top cover in five different ports. For direct contact with the solution, the transducer, which had a 1.5 cm diameter and a frequency of 1.7 MHz, was positioned at the bottom of the ultrasonic reactor. It should be noted that the transducer converts the electrical power into ultrasonic irradiation using the calorimetric method [32]. The procedure for conducting the CO₂ absorption experiments is comprehensively described in our previous research paper [21].

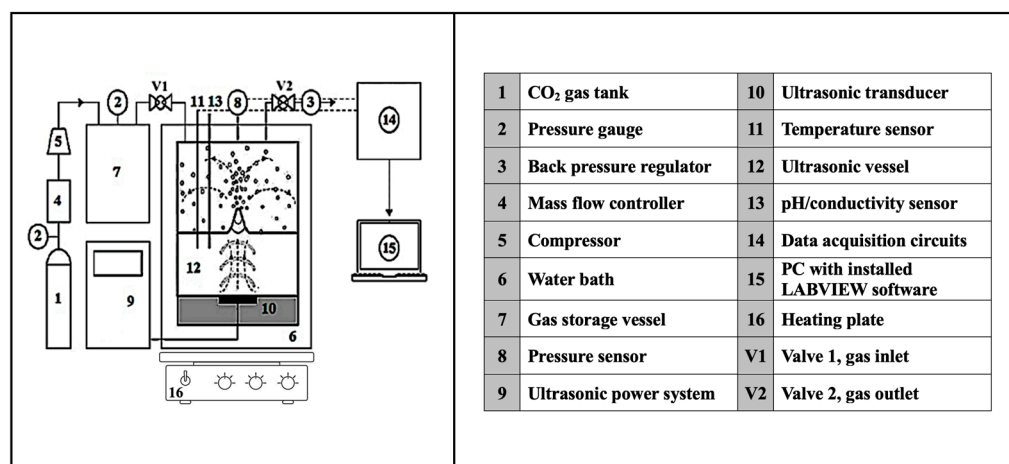


Figure 3. Schematic of the ultrasonic-assisted CO₂ absorption system.

3.3. Procedure of Reaction Pathway Evaluation

Various samples needed to be analyzed to provide sufficient analytical data for identifying the role of the sonochemical effect, in particular OH radicals, on the reaction pathway. The HPLC characterization technique was implemented for analysis. The analysis was performed by evaluating the significance of OH radicals during the CO₂ absorption process using

promoter-free MDEA. In line with this aim, in-vitro detection of OH radicals was performed. TA was used as the OH radical scavenger. The optimum mass concentration of TA to be used in the subsequent experiments was 10 wt%. It should be noted that the optimum mass concentration of TA is defined as the concentration necessary to trap all the generated OH radicals from the reaction mixture [33,34], which can subsequently inhibit the CO₂ absorption process without affecting the reaction pattern. The samples were divided into four groups, with each group being tested three times under two different conditions, including irradiated and non-irradiated. The samples are listed in Table 3. For each sample, the HPLC chromatograms were analyzed to identify the stable chemical compounds formed under different conditions. The identification of chemical compounds was performed based on the standard verification method. Subsequently, the concentration of the identified chemical compounds was calculated based on the HPLC peak area and HPLC calibration curves. Finally, to verify the mechanism, the reaction pathway was evaluated by comparing concentration variations between irradiated and non-irradiated samples.

Table 3. List of samples subjected to HPLC analysis.

Group No.	Sample Description
A	50 wt% aqueous MDEA
B	50 wt% aqueous MDEA + 10 wt% TA
C	50 wt% aqueous MDEA + CO ₂
D	50 wt% aqueous MDEA + 10 wt% TA + CO ₂

3.4. HPLC Equipment and Chromatographic Conditions

As mentioned in Section 3.3, the analysis of the scavenged OH radicals were performed by the HPLC instrument (Model Agilent series 1100). A YMC-Pack Polymer C18 reverse phase column (250 mm × 6.0 mm ID) was selected. The column was carefully washed with a mixture of water and acetonitrile (60:40) 1 h before and 2 h after use. The eluent was a mixture of 100 mM Na₂HPO₄ and 100 mM NaOH (ratio 60:40 at a pH of 12). The eluent flow rate was 0.6 mL·min^{−1}, and the analysis was conducted at 20 °C. The injection volume of the sample was 20 µL, and the UV light at a wavelength of 215 nm was used as the detector. For calibration purposes, two sets of standards with different concentrations were freshly prepared. The first set of calibration standards consisted of an aqueous solution of MDEA with concentrations of 10, 20, 30, 40, and 50 wt%. Since TA is poorly soluble in water, the second set of standards consisted of various mass concentrations of TA dissolved in the 50% aqueous MDEA solution. TA concentrations were 1, 3, 5, 7, 9, and 11 wt%. The different sets of the prepared standards were then injected into the HPLC system. For each set of calibration standards, the relationship between the peak area of the compound and its concentration was evaluated. The calibration curve for each set of standards was then plotted. Subsequently, the coefficient of determination (R²) was obtained from the regression line. The calibration curves for MDEA and TA with the respective R² values of 0.99 and 0.98 are presented in Figure 4.

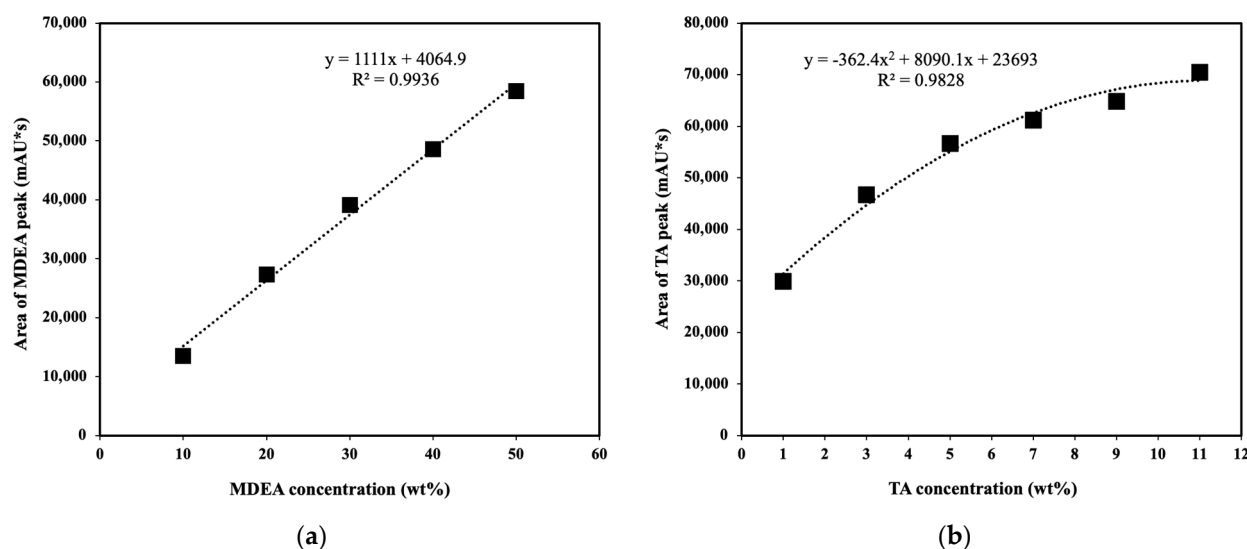


Figure 4. HPLC calibration curve and calibration equation for (a) MDEA, (b) TA.

4. Results and Discussion

As mentioned, four different groups of liquid-phase samples were chosen for analysis. Each group was examined under irradiated and non-irradiated conditions. Then the samples were characterized by the HPLC analytical technique with UV detection. According to the obtained HPLC data, stable chemical compounds formed under irradiated and non-irradiated conditions were identified. The final concentrations of the identified chemical compounds were calculated using the HPLC peak area and the calibration curves. The reaction pathway was finally evaluated by comparing the detected peaks, which represent the chemical compounds and their concentration variations between the two testing conditions. The results of the HPLC-UV characterization of the selected samples are as follows.

4.1. HPLC Analysis of Aqueous MDEA Solution

Two samples containing 50 wt% MDEA in the aqueous form were injected into the HPLC system. The ultrasonic irradiation was applied to the first sample (A1) but not to the second (A2). The ultrasonic power and the frequency were 12.36 W and 1.7 MHz, respectively. The chromatogram of these samples is shown in Figure 5. Firstly, the straight baseline was observed in both chromatograms, indicating the accuracy of the results. Moreover, one peak was observed in each chromatogram, representing the MDEA. The identity of the detected peak was validated by comparing it to previously tested MDEA standards. The obtained HPLC data is summarized in Table 4. The final concentrations of MDEA in both samples were determined based on the peak area and the HPLC calibration curve for MDEA, as shown in Figure 6. The same aqueous MDEA solution with the approximate initial concentration of 50 wt% was used for both samples. The results show insignificant changes in the final concentration and indicate the stability of MDEA molecules once irradiated by high-frequency ultrasonic irradiation. Such an insignificant rise in the concentration of the irradiated sample might be due to the possibility of minor evaporation of the water content of the aqueous solution during the high-frequency ultrasonic irradiation [35,36]. In particular, the evaporation is induced by the heating effect of ultrasonic irradiation. When the ultrasonic wave transmits to the liquid phase, some of the ultrasound energy is converted to heat energy, causing the liquid phase to heat up and evaporate. However, external cooling systems like an air fan, cooling water jacket, cooling coil, or water bath can maintain the liquid temperature and minimize evaporation [37].

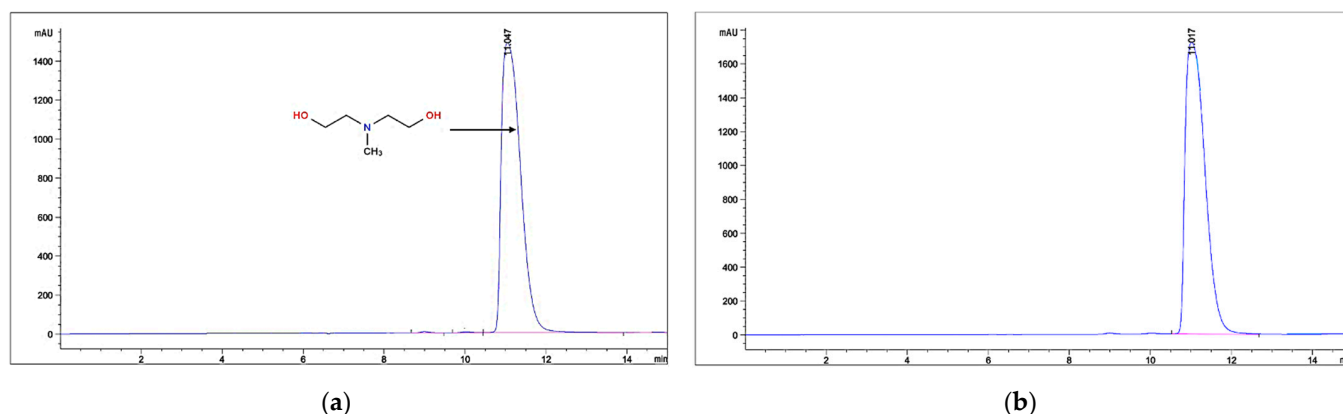


Figure 5. HPLC chromatograms of 50 wt% aqueous MDEA solution under different conditions (a) Irradiated, (b) Non-irradiated.

Table 4. Chromatographic data of aqueous MDEA solution.

Ultrasonic Power: 12.36 and 0 W, Initial [MDEA]: 50 wt%, Temperature: 70 °C Identification Method: HPLC-UV				
Sample No.	Condition	Observed RT of Peak [min]	Peak Area $\times 10^4$ [mAU $\times$ s]	Identity
A1	Irradiated	11.047	6.14	MDEA
A2	Non-irradiated	11.017	5.98	MDEA

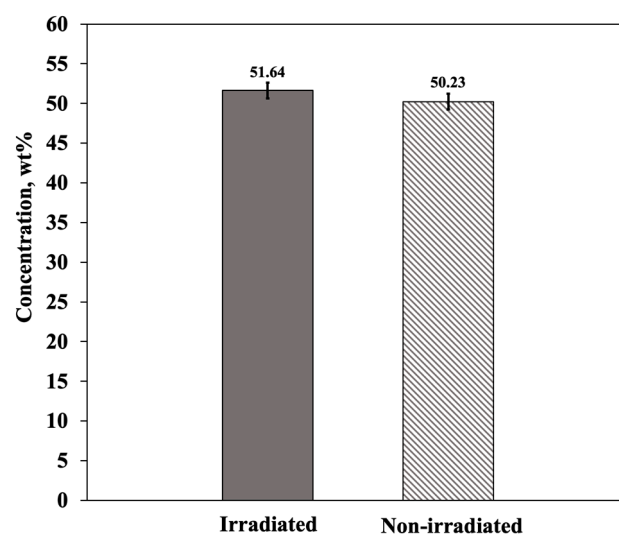


Figure 6. Concentration variation of aqueous MDEA solution under different testing conditions.

4.2. HPLC Analysis of Aqueous MDEA Solution Blended with TA

Similar to the previous step, two samples in the aqueous form containing 50 wt% MDEA blended with 10 wt% of TA were prepared for HPLC analysis. The ultrasonic irradiation was applied to the first sample (B1) but not to the second (B2). The HPLC chromatogram of these samples is shown in Figure 7.

According to Figure 7, two peaks were observed in each chromatogram, identified as TA and MDEA for the irradiated sample. However, it was expected to observe one more peak representing 2-hydroxyterephthalic acid (HTA), but due to the low concentration, the peak shape is a bit flat and cannot be observed. The concentrations of the identified peaks were determined based on the peak area, as mentioned in Table 5, and the HPLC calibration curve for MDEA and TA. The results are presented in Figure 8. Since the same peaks were detected in both samples and no additional peaks were observed, it can be stated that

ultrasonic irradiation did not change the structure of the mixture. Moreover, according to the results, no significant changes in the concentrations of the MDEA compound in both irradiated and non-irradiated samples were observed. However, the concentration of TA compound in the irradiated sample was lower than in the non-irradiated sample, indicating the presence of more OH radicals under the irradiated condition. These findings confirmed the stability of MDEA molecules; thus, it can be stated that the possibility of breaking the chemical bond of the MDEA molecule with high-frequency ultrasonic irradiation is negligible. In other words, the generation of OH radicals scavenged by TA might be due to the dissociation of the water content of the aqueous solution [38,39].

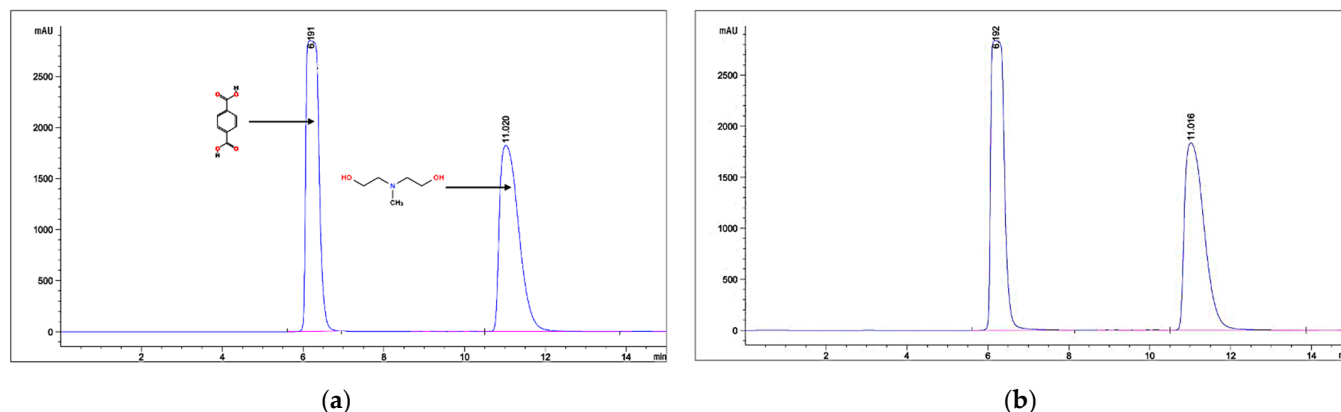


Figure 7. HPLC chromatograms of 50 wt% aqueous MDEA solution blended with 10 wt% TA under different conditions (a) Irradiated, (b) Non-irradiated.

Table 5. Chromatographic data of aqueous MDEA solution blended with TA.

Ultrasonic Power: 12.36 & 0 W, Initial [MDEA]: 50 wt%, Temperature: 70 °C Identification Method: HPLC-UV				
Sample No.	Condition	Observed RT of Peak [min]	Peak Area $\times 10^4$ [mAU $\times$ s]	Identity
B1	Irradiated	6.191	6.32	TA
		11.020	6.12	MDEA
B2	Non-irradiated	6.192	6.81	TA
		11.016	5.98	MDEA

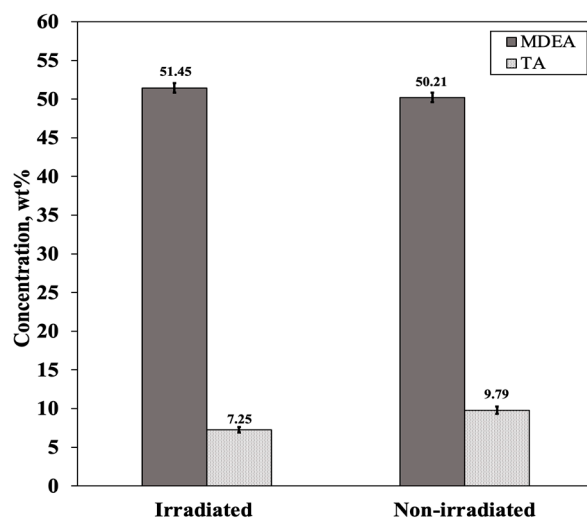


Figure 8. Concentration variation of aqueous MDEA solution blended with TA under different testing conditions.

The above-mentioned assumption can also be discussed from a molecular point of view. According to the molecular structure of MDEA, there are two O-H functional groups in the 1 and 1' positions, as shown in Figure 9. In each position, the O-H functional group is attached to a carbon atom, which is sterically hindered. Additionally, when atoms are close together, the energy of the covalent bonds that keep the atoms together in the molecule increases [40,41]. Due to the increased energy, breaking the chemical bond of the O-H functional groups of the MDEA molecule for generating OH radicals is more complex than in water, which is not considered a steric hindrance. Thus, the formation of OH radicals can be mainly attributed to the dissociation of water rather than MDEA.

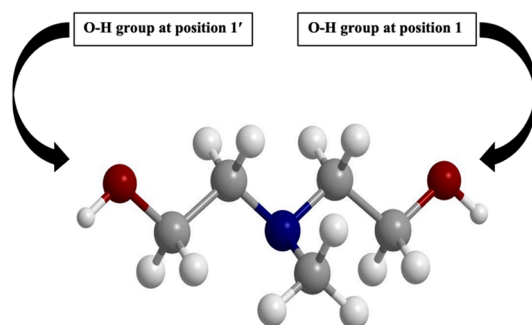


Figure 9. MDEA molecular structure (Gray, white, red, and blue balls represent C, H, O, and N atoms, respectively).

4.3. HPLC Analysis of the CO₂ Absorbed into the Aqueous MDEA Solution

The CO₂ absorption into the aqueous MDEA solution was also analyzed by HPLC under two different conditions to provide sufficient information for elucidating the role of the sonochemical effect on the chemical reactions. In the first approach, the CO₂ absorption process using promoter-free MDEA was performed in an ultrasonic-assisted reactor (C1). Whereas in the second approach, the CO₂ absorption process was carried out under the non-irradiated condition (C2). For both approaches, the experimental conditions were the optimized conditions obtained in our previous research work [21]. After the absorption process, the samples were injected into the HPLC equipment for analysis. The HPLC chromatogram and information of detected peaks are presented in Figure 10, and Table 6, respectively. Based on the retention time of the MDEA standards, one peak was identified as MDEA, but the other remained unidentified. The unknown peak might be any stable intermediate formed during the CO₂ absorption process utilizing MDEA aqueous solution, which can be identified further using the GC-MS characterization technique. However, the unknown peak was detected at a similar retention time in both testing samples, indicating that no change had happened to the sample after inducing ultrasonic irradiation. Therefore, due to the similarity of the presented peaks, it can be stated that no unexpected changes in terms of forming new chemical compounds occurred during CO₂ absorption into an aqueous MDEA solution in an ultrasonic-assisted reactor. According to the obtained data, the concentration of MDEA, as the identified peak, was calculated. Figure 11 shows the MDEA concentration changes for irradiated and non-irradiated samples after absorbing 11 bars of CO₂. The results showed no significant difference in the MDEA concentration of both samples, indicating that a similar amount of absorbent was consumed during the CO₂ absorption process.

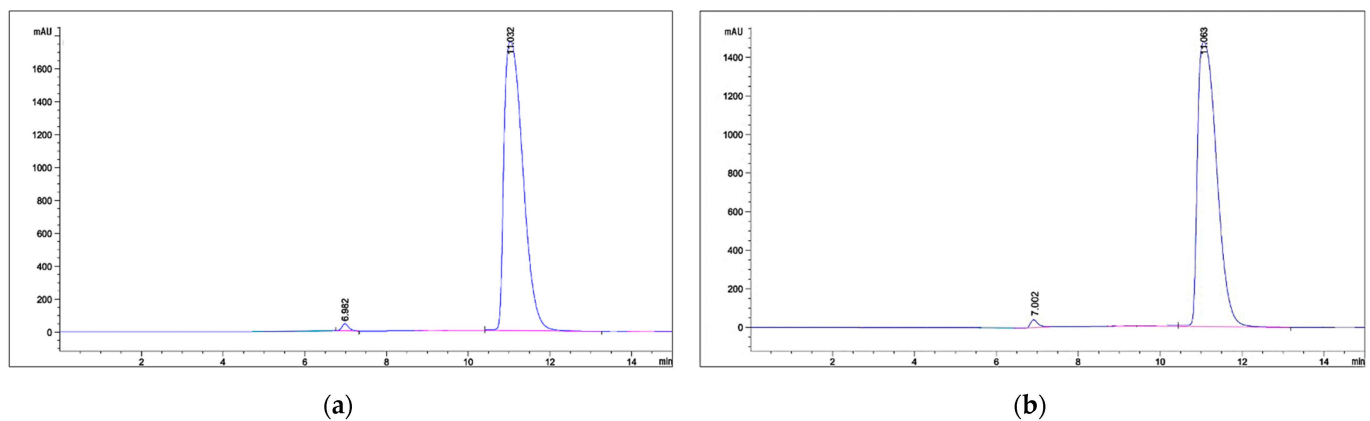


Figure 10. HPLC chromatograms of CO₂ absorption into aqueous MDEA solution under different conditions (a) Irradiated, (b) Non-irradiated.

Table 6. Chromatographic data of the CO₂ absorbed into aqueous MDEA solution.

Ultrasonic Power: 12.36 and 0 W, Initial [MDEA]: 50 wt%, Temperature: 70 °C, CO ₂ Pressure: 10 bar Identification Method: HPLC-UV				
Sample No.	Condition	Observed RT of Peak [min]	Peak Area $\times 10^4$ [mAU $\times$ s]	Identity
C1	Irradiated	11.032	5.64	MDEA
		6.982	0.052	Unknown
C2	Non-irradiated	11.063	5.43	MDEA
		7.002	0.055	Unknown

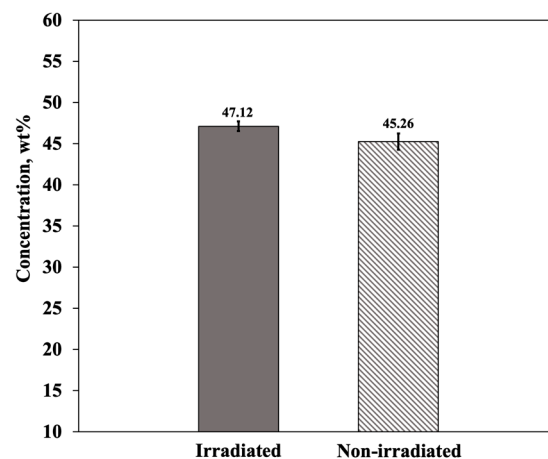


Figure 11. Concentration variation of aqueous MDEA solution after CO₂ absorption under different testing conditions.

4.4. HPLC Analysis of the CO₂ Absorbed into the Aqueous MDEA Solution Blended with TA

The CO₂ absorption process utilizing an aqueous MDEA solution was further investigated by HPLC in the presence of TA. The tests were performed under irradiated (D1) and non-irradiated (D2) conditions using a 50 wt% aqueous solution of MDEA mixed with 10 wt% TA. After the CO₂ absorption process, the samples were injected into the HPLC system. As previously stated, the operating conditions were set at the optimized experimental conditions for promoter-free MDEA. The HPLC chromatogram of the samples and the information about the detected peaks are presented in Figure 12 and Table 7, respectively.

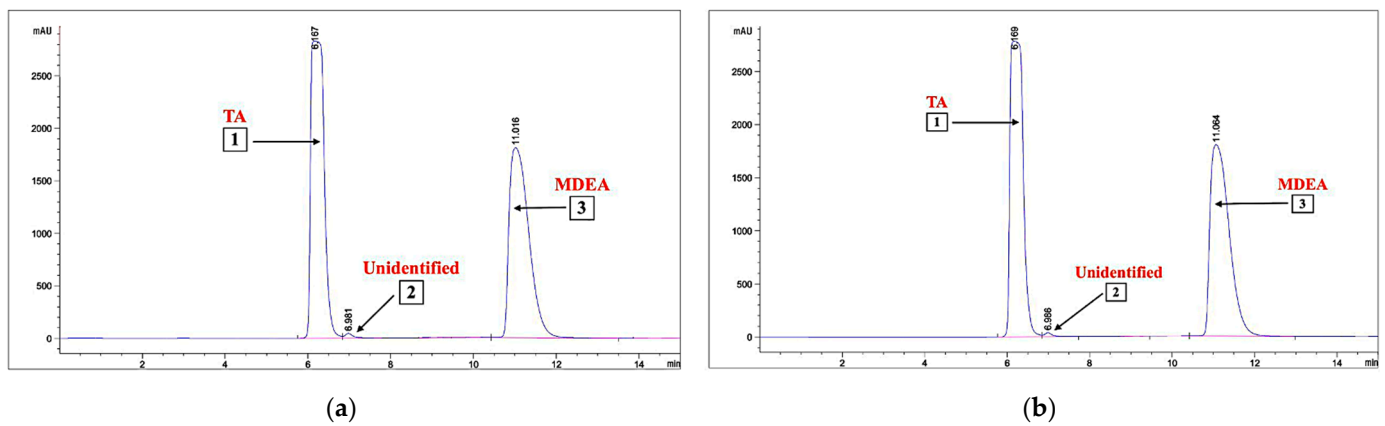


Figure 12. HPLC chromatograms of CO₂ absorption into aqueous MDEA solution mixed with TA under different conditions (a) Irradiated, (b) Non-irradiated.

Table 7. Chromatographic data of the CO₂ absorbed into aqueous MDEA solution mixed with TA.

Ultrasonic Power: 12.36W, [MDEA]: 50 wt%, [TA]: 10 wt%, Temperature: 70 °C, Pressure: 10 bar Identification Method: HPLC-UV					
Sample No.	Condition	Peak Number	Observed RT of Peak [min]	Peak Area $\times 10^4$ [mAU $\times$ s]	Identity
D1	Irradiated	1	6.167	6.43	TA
		2	6.981	0.06	Unknown
		3	11.018	5.84	MDEA
D2	Non-irradiated	1	6.169	6.81	TA
		2	6.986	0.05	Unknown
		3	11.064	5.55	MDEA

As can be seen, in each chromatogram, three peaks were observed. According to the retention time and referring to the calibration standards, the MDEA and TA peaks were identified. But the second peak in both samples could not be identified. Nevertheless, the retention time of the unknown peak was almost similar in both samples, indicating the formation of an identical compound. Due to the similarity of the observed peaks in both irradiated and non-irradiated conditions, it can be stated that the CO₂ absorption performed in almost the same way. In both conditions, the concentrations of the identified peaks, MDEA and TA, were calculated based on the respective calibration curves. Figure 13 shows the concentration variation of the identified peaks for irradiated and non-irradiated samples. For the sample tested under the non-irradiated condition, the concentration of TA is approximately equal to the initial concentration of 10 wt%, indicating that the formation of OH radicals is not feasible under the non-irradiated condition. Conversely, the variation in TA concentration in the irradiated sample confirmed the presence of OH radicals and their involvement during the CO₂ absorption process. Furthermore, there were no significant differences in MDEA concentrations for the irradiated sample compared to the scavenger-free CO₂ absorption process (C1). The insignificant concentration variations of MDEA support the idea of MDEA molecular stability versus water molecules under high-frequency ultrasonic irradiation. Thus, the scavenged OH radicals during the CO₂ absorption originated insignificantly from the breakage of the MDEA chemical bonds. In other words, the formation of OH radicals seems to be predominantly caused by the dissociation of water molecules, which may eventually assist in the CO₂ absorption process.

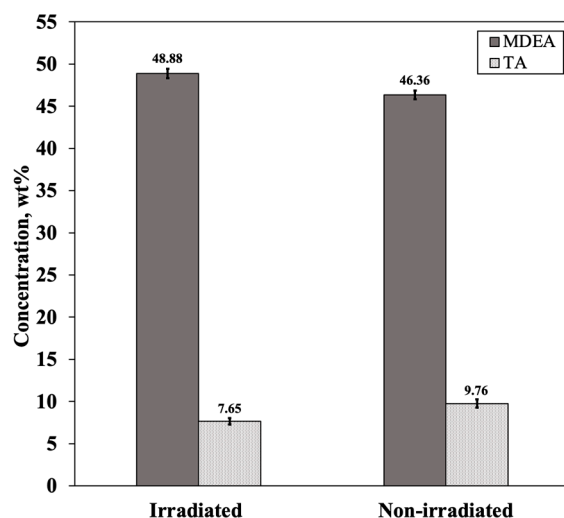


Figure 13. Concentration variation of MDEA and TA under different conditions after CO₂ absorption.

4.5. Evaluation of the Reaction Pathway

According to the HPLC characterization results of the samples, no new chemical compounds were detected during the CO₂ absorption process utilizing MDEA in the high-frequency ultrasonic-assisted reactor. Thus, the hypothesis of changing the reaction pathway due to the presence of the sonochemical effect is invalid. The stability of MDEA molecules compared to water molecules explains the non-alteration in the reaction pathway despite inducing high frequency and high power ultrasonic irradiation. It means that the applied ultrasonic energy can readily break the water molecules but not the MDEA molecules. Even if the MDEA molecules partially break down and release OH radicals, they would immediately react with the available OH radicals and reestablish themselves since they are in an irradiated aqueous solution with abundant OH radicals. Thus, it can be stated that despite the presence of the sonochemical effect, the reaction of CO₂ absorption into aqueous MDEA solution can still be explained by the conventional reaction pathway shown in Figure 14.

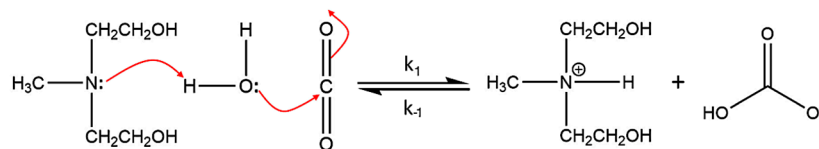
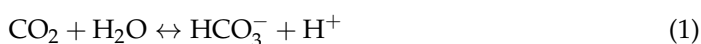


Figure 14. The reaction mechanism of CO₂ absorption into aqueous MDEA solution.

According to the conventional reaction pathway, MDEA, as a tertiary alkanolamine, cannot directly react with CO₂ as it has no hydrogen atom attached to the nitrogen atom. It is worth noting that the presence of hydrogen atoms is essential for a direct reaction with CO₂. Due to the lack of hydrogen and, consequently, proton, MDEA can provide a sink for the hydrogen ions produced when CO₂ hydrolysis in water to form bicarbonate. The complete mechanism includes three reactions [42]:



Therefore, while the sonochemical effect cannot change the reaction pathway, in the aqueous solutions, it can accelerate the generation of OH radicals via water sonolysis. In

particular, for the above reactions, such acceleration could alter the slow formation of bicarbonate, resulting in a faster rate of CO₂ absorption.

4.6. Significance of Ultrasonic Irradiation on CO₂ Absorption Rate

The sonochemical effect can significantly influence the rate of CO₂ absorption. To clarify its influence, the CO₂ absorption rate was assessed in the absence and presence of TA (as the scavenger for OH radicals) operating under irradiated and non-irradiated settings. The basis of rate determination is explained in our previous research work [21]. The findings are shown in Figure 15. The absorption rate under the non-irradiated condition remained approximately unchanged in both the presence and absence of TA. Whereas for the irradiated condition, it changed considerably. In an irradiated setting and without TA, the CO₂ absorption rate was about 4.20 mol/h. However, the CO₂ absorption rate was reduced to 0.75 mol/h by adding TA. The 5.6-fold reduction can explain the significance of the sonochemical effect on absorption rate enhancement. Thus, despite the non-alteration of the reaction pathway, the generated OH radicals induced by the sonochemical effect can significantly influence the CO₂ absorption rate.

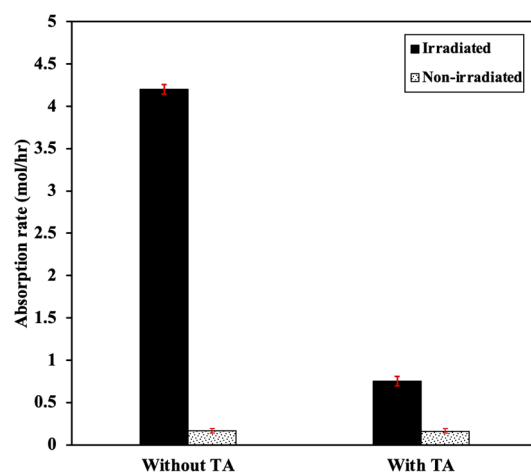


Figure 15. Experimental absorption rate of different systems using 0 and 12.36 W ultrasonic power, CO₂ initial pressure of 11 bar, temperature of 70 °C, MDEA concentration of 50 wt%, and TA concentration of 10 wt%.

5. Conclusions

Ultrasonic irradiation is a novel technique that can intensify the CO₂ absorption process because of the sonochemical and sonophysical effects. The fundamental principles of sonophysical and sonochemical effects in assisting CO₂ absorption have been proven recently. Nevertheless, more detailed research is still needed to light up the path of commercial use of ultrasonic-assisted CO₂ absorption systems. Particularly, it is crucial to investigate the significance of the sonochemical effects on the chemical reactions of the CO₂ absorption process. It is hypothesized that the sonochemical effect might affect the chemical reactions either by accelerating or altering them. Therefore, to assess the above-mentioned assumptions, the role of the sonochemical effect on the reaction pathway was evaluated by analyzing various samples. The sample analysis was performed by evaluating the importance of OH radicals during the CO₂ absorption process using promoter-free MDEA. Moreover, TA was used as the potential OH radical scavenger. For each sample, chemical components from the liquid phase were analyzed by HPLC and compared under irradiated and non-irradiated conditions. The comparison aimed to find possible evidence of the sonochemical effect's capability to change the reaction pathway. The similarity of the comparative results claimed that the sonochemical effect could not change the reaction pathway. Thus, the admitted origin of sonochemistry in aqueous solutions was water sonolysis, which could generate the OH radicals and subsequently accelerate the CO₂ absorption process.

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Nomenclature

bar	Pressure unit
BC	Bubble column
CO	Carbon monoxide
CO ₂	Carbon dioxide
DC	Disk column
DEA	Diethanolamine
HFMFC	Hollow fiber membrane contactor
HFUA	High-frequency ultrasonic assisted
HPLC	High-performance liquid chromatography
H ₂ S	Hydrogen sulfide
ID	Inner diameter
K	Temperature unit, Kelvin
K ₂ CO ₃	Potassium carbonate
mAU	milli-Absorbance Unit
M	Molar
MC	Microchannel
MEA	Monoethanolamine
MHz	Megahertz, frequency unit
MDEA	Methyl diethanolamine
NaOH	Sodium hydroxide
Na ₂ CO ₃	Sodium carbonate
nm	Nanometer, wavelength unit
OH	Hydroxyl radical
PB	Packed bed
RPB	Rotating packed bed
RT	Retention time
TA	Terephthalic acid
T	Temperature
UV	Ultraviolet spectroscopy
W	Watt, ultrasonic power unit
WWC	Wetted wall column

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