

Research Article

Sustainable MWCNT and TiO₂ Nanofluids for CO₂ Absorption and Their Stability: An Experimental Study

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Abstract

Carbon dioxide (CO₂) emissions contribute significantly to global warming. To mitigate this issue, various technologies are being explored for CO₂ capture and storage. One such method involves direct contact absorption using nanofluids. In this research, the preparation of sustainable MWCNT and TiO₂ nanofluids, their stability and usage of these nanofluids for CO₂ absorption application have been discussed. Sustainable nanofluids are the materials widely used in the heat and mass transfer and energy storage applications, etc., but it is important to have higher stability by following the right approach of preparation of nanofluids. CO₂ absorption performance of MWCNT and TiO₂ nanofluids at 0.03, 0.06, 0.09 and 0.12 wt% concentrations was evaluated as compared to basefluid DI water and tested at initial pressures of 5, 7.5 and 10 bar inside the absorption cell. The stability of the nanofluids was assessed using Zeta Potential and UV-spectroscopy. Results showed that increasing the concentration of nanofluids generally enhanced CO₂ absorption capacity, but there was an optimal concentration beyond which the trend reversed. For the given conditions, 0.03 wt% of MWCNT and 0.09 wt% of TiO₂ nanofluids exhibited the highest CO₂ absorption capacity. As compared to basefluid DI water, MWCNT nanofluid at 0.03 wt% concentration improved CO₂ absorption by 22.54%, 30.16%, and 34.35% at 5, 7.5, and 10 bar, respectively. Similarly, TiO₂ nanofluid at 0.09 wt% concentration increased CO₂ absorption by 17.84%, 23.9%, and 25.85% at the same pressures. The enhanced CO₂ absorption performance of the nanofluids is attributed to micro-convection and shuttle effects caused by the nanoparticles. The high negative Zeta Potential values (-39.5 mV for MWCNT and -42.8 mV for TiO₂) indicated excellent stability of the nanofluids. The nanofluids demonstrated good stability, maintaining their properties even after four weeks of preparation.

Keywords: CO₂ absorption, MWCNT, Stability of nanofluids, TiO₂, Zeta Potential

1 Introduction

Carbon dioxide (CO₂) gas emissions have increased over the years and it is the reason for the global warming effect. Many countries, including the European Union have come forward to reduce the amount of CO₂ being emitted into the atmosphere before 2035 under the Kyoto Protocol and Paris agreement [1]–[5]. To reduce the emission rate of CO₂, one method is separation and collection, utilization and storage [6]. To limit CO₂ emissions, the Carbon Capture and Storage (CCS) technique has played a significant role. Out of the several separation methods, absorption, adsorption, cryogenic, and membrane contact separation are the important technologies used in CO₂

capture [6]–[8]. Some progress has been made in CO₂ absorption by using solvents. Water, amines, nanofluids, ammonia and NaCl solutions can be used as solvents [9], [10]. This method has better performance when nanoparticles are added to the basefluids. Since the nanoparticles have got higher surface area, the CO₂ absorption will be enhanced. One of the challenges of this process is to minimize the energy consumed during the CO₂ absorption process [11]. The CO₂ gas absorbed by the solvent is referred to as the absorbate, while the solvent that absorbs the gas is known as the absorbent. Amine solvents also have better absorption performance due to their high thermal stability, high capacity and high reaction rate with CO₂ molecules [12]. Monoethanolamine (MEA), diethanolamine (DEA),

and methyldiethanolamine (MDEA) are some of the amines that can be used as absorbents. Over the last few years, nanofluids have been demonstrated for their applications in CO₂ absorption due to their adjustable chemical, physical properties and higher surface area [13]. The basefluid used for the preparation of nanofluids can be water, methanol, ethanol, amines, etc.

Many industries like chemical, medicine, machinery, aerospace and energy are being benefitted with the use of nanofluids. It was found that the use of small quantities enhances the gas absorption rate. It was investigated that the absorption increased by 22.3% and 39.8% respectively, compared to the basefluid for Al₂O₃ and TiO₂ nanofluids [7]. When nanofluids are used for CO₂ absorption, the variables that affect the CO₂ absorption are nanofluid concentration, nanoparticles size, morphology, surface area of particles, type of nanoparticles, type of basefluids, stability of nanofluids, initial pressure and temperature. By using SiO₂/water and CNT/water nanofluids, a numerical investigation was carried out to evaluate the enhancement of CO₂ absorption rate as compared to the basefluid and it was observed to be at 18% and 47%, respectively [14]. The experiments were conducted in a packed bed column in which CO₂ gas was used as the absorbate and NiO and Fe₃O₄ nanofluids were used as absorbents. The results found that CO₂ absorption enhancement was 9.5% and 12% respectively. It was found that an increase in concentration enhances the CO₂ absorption and there is an optimum concentration. Any further increase beyond this, the CO₂ absorption rate diminishes. The optimum concentration for NiO was 0.005 wt% and for Fe₃O₄ was 0.01 wt% [15]. ZnO/water and SiO₂/water nanofluids were used in a stirred vessel at 2, 5 and 8 °C temperatures. The CO₂ enhancement was 14% for ZnO nanofluid and 7% for SiO₂ nanofluid at 0.1 wt% [16]. A direct contact CO₂ absorption test was conducted for SiO₂, Fe₂O₃, Al₂O₃ and CNT nanofluids at 20, 30 and 40 bar as initial pressure, 308 K of temperature, with concentrations of 0.02, 0.05 and 0.1 wt%. The CO₂ absorption capacity of nanofluids was enhanced by 18% and 21% for Al₂O₃ and SiO₂ at 0.1 wt%, respectively. For Fe₂O₃ and CNT, the CO₂ enhancement was 24% and 34%, respectively, at 0.02 wt%. The effect of initial pressure CO₂ absorption was also investigated. It was found that the higher the initial pressure, the higher the absorption capacity [17]. Methanol based Al₂O₃ and SiO₂ nanofluids were used in a bubble column to measure the CO₂ absorption at concentrations of 0.005 to 0.5 vol% and 20 °C. It was enhanced by 4.5% for Al₂O₃ nanofluid and 5.6% for SiO₂ nanofluid at 0.01 vol% [18]. The

order of absorption capacity of nanofluid is CNT > Fe₂O₃ > TiO₂ > SiO₂ > Al₂O₃ [19]. Monoethanolamine (MEA) and ethylenediamine (EDA) based graphene oxide (GO) nanofluid has been used to measure the CO₂ absorption rate in a hollow fiber membrane contactor at 0 to 0.5 wt% at 25 °C. The CO₂ absorption was enhanced by 49% for GO-MEA and 34% for GO-EDA at 0.2 wt%. BES analysis was conducted to measure the surface area of nanoparticles [20]. Methyldiethanolamine (MDEA) based magnetic GO nanofluid was experimented to determine the enhancement of CO₂ absorption and heat transfer. FTIR, SEM, XRD, TEM and BET studies were conducted for the characterization of nanoparticles. There has been a 37% increase in the CO₂ absorption capacity of nanofluid [21]. CFD simulation was carried out in high pressure stirred vessel for DI water based TiO₂ nanofluids at various concentrations. 0.1 wt% was found to be the optimum concentration. The enhancement was found to be 27% at 0.1 wt% [22]. Experimental and numerical studies were conducted to investigate the effect of nanofluids on CO₂ absorption in a hollow fiber membrane contactor. The results have shown that there was a 12.2% enhancement at 0.02 vol% [23]. From the results, it can be concluded that indeed the addition of nanoparticles enhances the absorption capacity of the basefluid. The mechanisms leading to enhancement are Brownian motion, Shuttle (Grazing) effect, Bubble breaking effect and micro-convection effect. The shuttle effect is gas absorption by particles that can penetrate the gas-liquid membrane to absorb higher amounts of CO₂ gas. Nanoparticles carrying absorbed CO₂ gas move to the bulk liquid and then desorb due to the concentration difference [24], [25]. From the literature, velocity disturbance is the main reason for absorption enhancement [24], [26], [27]. During the absorption process, collision of particles and particles with bubbles occurs. These bubbles move towards the gas-liquid interface and particles strike the interface, and this will result in breaking the bubbles and thereby increasing the mass transfer coefficient [28]–[30]. Micro-convection is due to the Brownian motion of nanoparticles, which results in the enhancement of mass transfer and it is mainly enhanced by fluid disturbance [31]–[33]. The stability of the nanofluids also plays an important role in heat and mass transfer applications. The higher the stability of nanofluids, the CO₂ absorption enhancement will be better [4], [34]. If the stability of nanofluids is less, all the nanoparticles would be agglomerated and settled at the bottom of the vessel [35], [36].

There are no studies conducted on TiO_2 and MWCNT nanofluids at 0.03, 0.06, 0.09 and 0.12 wt% and 5, 7.5 and 10 bar initial pressure for the application of CO_2 absorption. Additionally, no prior research has examined the stability of nanofluids after preparation and after 4 weeks of preparation using zeta potential and UV spectroscopy. Furthermore, no studies were made available for MWCNT nanofluid having higher stability by considering the right surfactant. To address these gaps, this research employs a direct contact method to investigate the CO_2 absorption capacity of DI water based MWCNT and TiO_2 nanofluids. This work investigates the influence of nanofluid concentration and nanoparticle type on CO_2 absorption capacity. Additionally, the stability of MWCNT and TiO_2 nanofluids was examined using Zeta Potential and UV-Vis spectroscopy immediately after preparation and after 4 weeks of preparation.

2 Materials and Methods

The MWCNT and TiO_2 nanoparticles are procured from Sigma Aldrich. The properties of these nanoparticles are shown in Table 1. The CO_2 gas used for experimentation has 99% purity and 1% humidity. The SEM studies were performed for these nanoparticles to check the size of the particles. Figures 1 and 2 show an SEM image of MWCNT and TiO_2 nanoparticles.

Table 1: Properties of MWCNT and TiO_2 .

Properties	MWCNT	Properties	TiO_2
Purity	99.9%	Purity	99.9%
Number of layers	4–8	Average particle size	30–80 nm
Inner diameter	5–10 nm	Molecular weight	80 g/mol
Outer diameter	10–30 nm	Bulk density	0.35g/cm ³

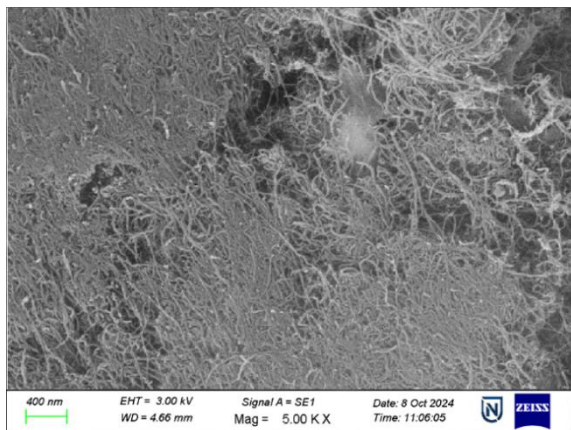


Figure 1: SEM image of MWCNT nanoparticles.

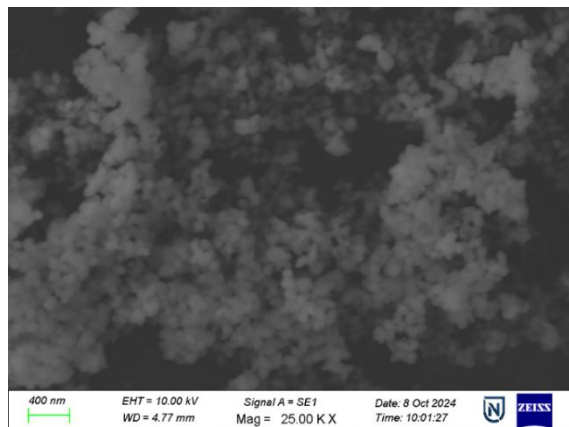


Figure 2: SEM image of TiO_2 nanoparticles.

2.1 Preparation of nanofluids

The nanofluids were prepared in 120 mL of DI water, which was used as the basefluid. The concentrations considered are 0.03 wt%, 0.06 wt%, 0.09 wt% and 0.12 wt%. The right quantity of weighed TiO_2 and MWCNT nanoparticles were taken as per the concentration. 20 min of magnetic stirring at 1000 rpm is performed, followed by 100 min and 120 min of sonication for TiO_2 and MWCNT nanofluids, respectively. Sonication has been performed to ensure the nanoparticles are uniformly distributed in the basefluid. As MWCNT nanoparticles are hydrophobic in nature and there is a need to add a surfactant. Initially, it was prepared using Sodium Dodecyl Benzene Sulfonate (SDBS) as surfactant, however, the stability of MWCNT nanofluids was less after 7 days. This forced us to use Gum Arabic as a surfactant. The surfactant enhances the stability even after 20 days of preparation. TiO_2 nanoparticles are hydrophilic in nature and hence no need to add surfactant. Figures 3 and 4 show the nanofluid samples of MWCNT and TiO_2 , respectively.

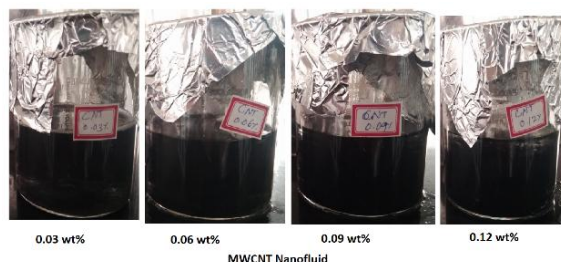
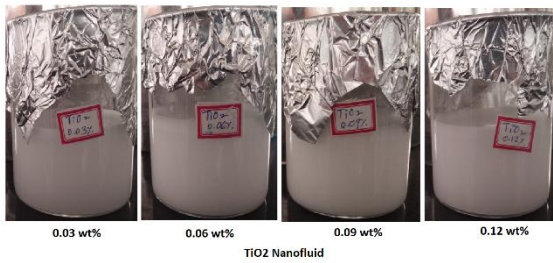
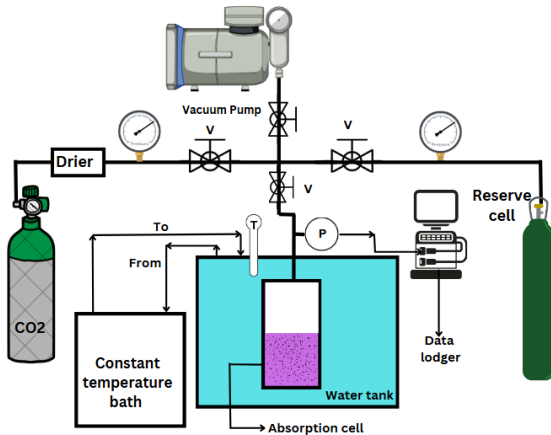


Figure 3: MWCNT nanofluid.

Figure 4: TiO₂ nanofluid.Figure 5: Direct contact CO₂ absorption experimental setup.

2.2 Experimental setup

The research employed a direct contact method for the methodology. A stainless-steel absorption cell was used due to its ability to endure higher pressures. The cell has a capacity of 300 cc, with 120 cc filled with nanofluid and the remaining 180 cc occupied by CO₂ gas above the nanofluid. A Danfoss MBS 3000 pressure transducer with an accuracy of ± 1 Pa was connected to monitor pressure changes over time. To maintain uniform temperature during the absorption process, a water bath was utilized, keeping the temperature constant at 300 K. Temperature measurements were taken using a K-type thermocouple. The schematic of the experimental setup is depicted in Figure 5. A vacuum pump was employed to remove air from the nanofluid's surface inside the absorption cell. A reserve cell was used to store CO₂ gas from the main cylinder at a pressure of 25 bar before transferring it into the absorption cell. The CO₂ gas used had a purity of 99%. The experimental system underwent a leakage test by applying soap solution to all joints, ensuring no leaks

in the setup. The pressure will drop as the CO₂ absorption takes place in the nanofluid. The decrease in pressure inside the absorption cell was recorded at an interval of 20 mins until the absorption process attains saturation. It was saturated at 150 min. The initial pressure maintained was 10 bar. The experiments were conducted for 7.5 and 5 bar initial pressures. The experiments were mainly conducted until the saturation state.

2.3 Data deduction

2.3.1 Absorption performance

To evaluate the CO₂ absorption performance of a nanofluid, the moles of CO₂ absorbed are measured using the changes in pressure within a custom absorption cell. As CO₂ enters the nanofluid, the pressure inside the cell decreases, and this pressure drop is used to calculate the amount of CO₂ absorbed. Equation (1) calculates the CO₂ absorption capacity of nanofluid per kilogram of nanofluid by considering the pressure drop inside the absorption cell. It represents its absorption capacity. This value provides a key indicator of how efficiently the nanofluid can absorb CO₂ over a specific period. It typically relies on principles from thermodynamics, such as the ideal gas law or specialized models specific to the experimental setup, which account for pressure, volume, and temperature changes.

$$\alpha = \frac{V_g}{R \times V_{liq} \times \rho_{liq} \times 300} \left[\frac{P_0}{Z_0} - \frac{P_t}{Z_t} \right] \quad \text{mol/kg} \quad (1)$$

where, α = Moles of CO₂ absorbed per kg of nanofluid, V_g = Volume of gas in absorption cell, P_0 = Initial pressure of CO₂ in absorption cell, P_t = Pressure at different intervals of time, Z_0 and Z_t = Compressibility factor initially and at different intervals of time, R = Universal gas constant, V_{liq} = Volume of nanofluid in absorption cell, ρ_{liq} = Density of nanofluid. The compressibility factor (Z) for CO₂ is determined using the Redlich-Kwong equation of state, particularly when the gas temperature surpasses its critical point. This equation relates the gas's volume, temperature, and pressure, providing an accurate model for real gas behavior under non-ideal conditions, such as high pressure or temperature. It helps account for deviations from ideal gas assumptions in these scenarios. The Relative Absorption Index (RAI), expressed in Equation (2), measures the improvement in CO₂ absorption

performance of nanofluids when compared to deionized (DI) water. This index is vital for assessing the enhanced efficiency of nanofluids in CO₂ capture. To ensure the reliability and consistency of the experimental results, repeatability is a key factor in the experimental process, confirming that the findings are robust and dependable across multiple trials.

$$RAI = \frac{\alpha_{nf} - \alpha_w}{\alpha_w} \quad (2)$$

where, α_f = Nanofluid, α_w = DI water

3 Results and Discussion

DI water based MWCNT and TiO₂ nanofluids are prepared at 0.03, 0.06, 0.09 and 0.12 wt%. The experiments were conducted by keeping the initial pressure of 5, 7.5 and 10 bar separately. The CO₂ absorption performance of nanofluids is evaluated by considering the pressure change at different intervals of time. The experiment was conducted until absorption was saturated in the nanofluid. The absorption is compared with basefluid under the same conditions.

3.1 Impact of nanofluid concentration

The nanofluid concentration impacts the absorption performance. From the experimental results, it was found that an increase in the concentration of TiO₂ nanofluid increases the CO₂ absorption capacity. It is surface phenomena where the higher the concentrations, the higher will be the surface area available for absorption of CO₂ gas. Figure 6(a)–(c) show the absorption capacity of TiO₂ nanofluid at initial pressures of 5, 7.5 and 10 bar, respectively. From the results, it can be observed that further increase in concentration decreases the absorption capacity of nanofluids, leading to restricted Brownian motion and higher viscosity of nanofluids. For TiO₂ nanofluid, it was found that 0.09 wt% is the optimum concentration. Since TiO₂ nanoparticles are hydrophilic in nature, particles attract water molecules, and these molecules occupy the surface of nanoparticles, which will decrease the surface area available for absorption of CO₂. These are the reasons for the decrease in absorption at higher concentrations of TiO₂. Figure 7(a)–(c) shows the absorption capacity of MWCNT nanofluid at initial pressures of 5, 7.5 and 10 bar, respectively. For MWCNT nanofluid, 0.03 wt% concentration has shown the highest absorption capacity as compared to other concentrations. Further

increase in the concentration of MWCNT nanofluid, CO₂ absorption decreased. This is because MWCNT nanoparticles are hydrophobic in nature, which repel water molecules and stability of nanofluids is the issue at higher concentrations [7], [9]. If the nanofluids are unstable, the nanoparticles accumulate at the bottom of the vessel. Brownian motion of nanoparticles will be restricted due to instability [22], [24].

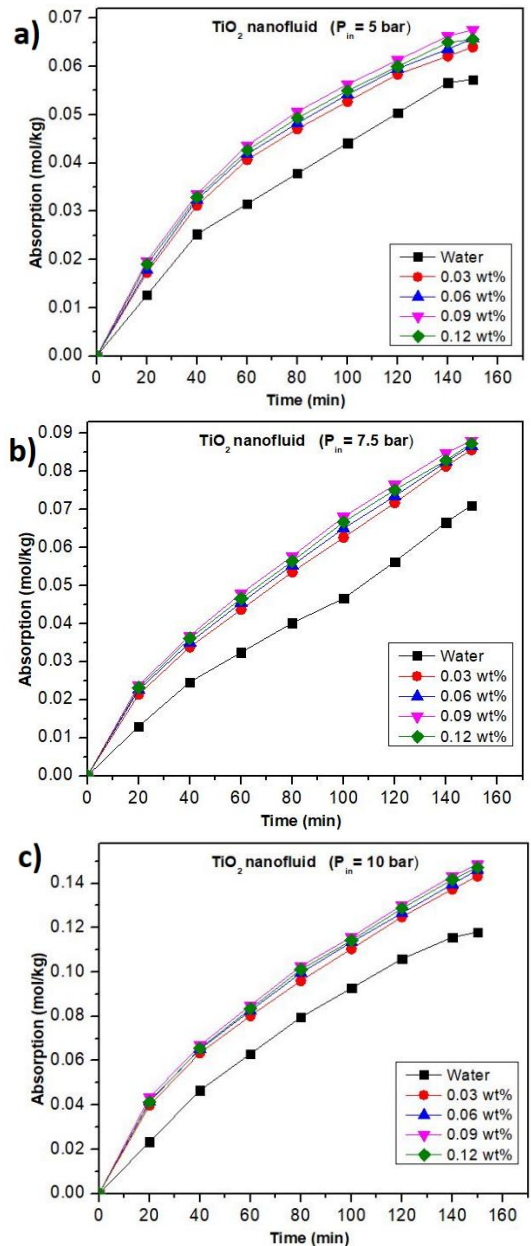


Figure 6: Absorption by TiO₂ at (a) 5 bar, (b) 7.5 bar and (c) 10 bar.

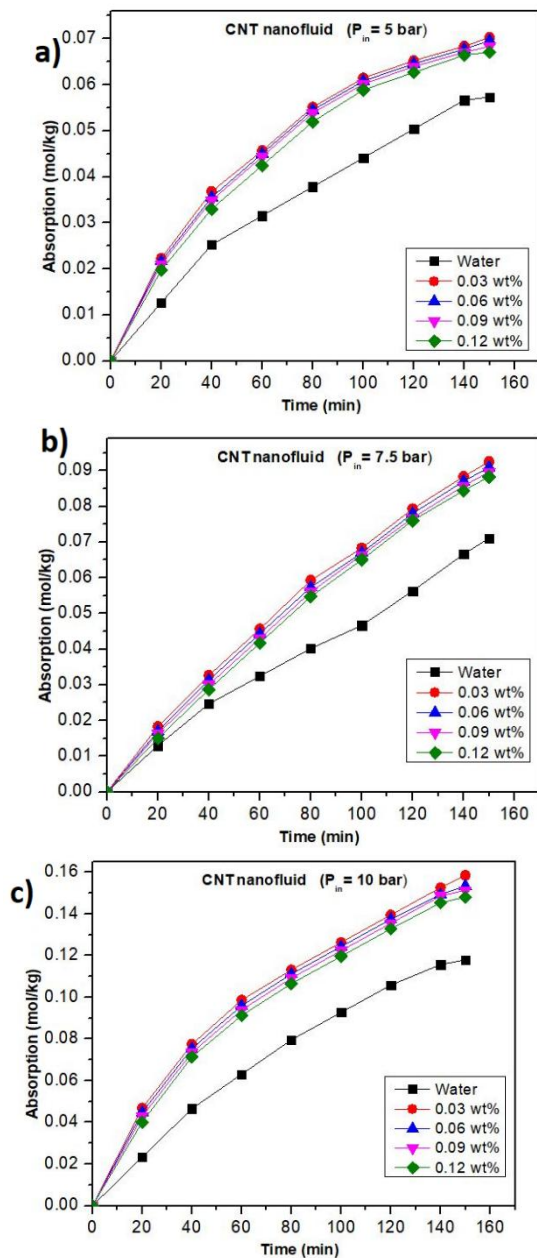


Figure 7: Absorption by MWCNT at (a) 5 bar, (b) 7.5 bar and (c) 10 bar.

From these nanofluids, it can be observed that hydrophobic nanofluids show better absorption as compared to hydrophilic nanofluids at similar conditions. Later, the CO₂ absorption performance of nanofluids has been compared to base fluid by using a parameter called the Relative Absorption Index (RAI). Figure 8(a)–(c) shows RAI for TiO₂ and MWCNT nanofluids at 5, 7.5 and 10 bar initial pressures,

respectively. It can be observed that the absorption capacity was enhanced by 17.84%, 23.9% and 25.85% due to the addition of TiO₂ nanoparticles at 0.09 wt% at 5, 7.5 and 10 bar, respectively. For MWCNT nanofluids, the absorption capacity was enhanced by 22.54%, 30.16% and 34.35% at 0.03 wt% at 5, 7.5 and 10 bar, respectively, as compared to the basefluid. Any further increase in nanofluid concentration beyond the optimum concentration, the CO₂ absorption performance of the nanofluid decreased.

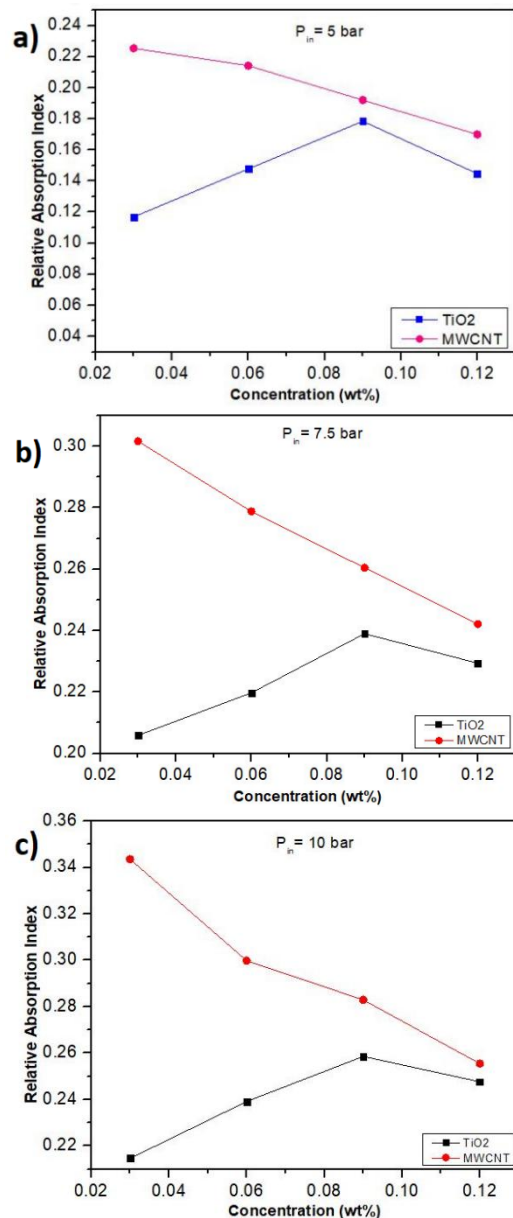


Figure 8: RAI at (a) 5 bar, (b) 7.5 bar, and (c) 10 bar.

3.2 Mechanism of CO₂ absorption enhancement

Few theories have been discussed about the mechanisms behind the enhancement of CO₂ absorption capacity of nanofluids. These mechanisms are micro-convection effect, shuttle effect and Brownian motion of nanoparticles. The shuttle effect is where CO₂ gas is adsorbed on the nanoparticle's surface area at the gas-liquid interface. Those nanoparticles are returning to the bulk liquid where the gas concentration is low [27]. The nanoparticles desorb the gas into the liquid and a fresh particle is regenerated. This particle again moves towards the gas-liquid interface for adsorption due to Brownian motion. This process continues where the particles are moving between higher and lower gas concentration regions, and it is called as shuttle or grazing effect. Another reason is the Brownian motion of nanoparticles, which is the random motion of particles within the basefluid and colliding with neighboring particles [8].

3.3 Stability analysis of nanofluids

Since the nanoparticles are dispersed in the basefluid, it is important to have nanoparticles uniformly dispersed in the basefluid for higher stability. As nanofluids are widely used in heat and mass transfer applications, which involve surface phenomena, the stability plays an important role in the improvement of the system. If the stability of the nanofluids is less, the nanoparticles would be agglomerated in the basefluid. The stability of nanofluids depends upon the types of nanoparticles, concentration, size of the particles, type of basefluid and type of surfactant used. Optimizing these parameters can enhance nanofluid stability, making zeta potential measurements a reliable method for predicting and improving the long-term usability of nanofluids in applications. The equipment available to measure the stability of nanofluids is the Zeta Potential. It is a key parameter in understanding the stability of nanofluids. It represents the electric potential at the slipping plane of a particle suspended in a fluid, essentially quantifying the repulsive forces between particles. High zeta potential values, either positive or negative, indicate strong electrostatic repulsion, which helps prevent particles from aggregating. This dispersion stability is crucial for maintaining the uniform distribution of nanoparticles within a fluid. If the zeta potential magnitude exceeds approximately ± 30 mV, the repulsive forces generally dominate, leading to stable colloidal systems [17].

Conversely, lower zeta potential values result in weaker repulsion and a greater likelihood of particle agglomeration or sedimentation, compromising the performance of the nanofluid. The higher the stability, the higher the CO₂ absorption capacity. In this research work, Zeta Potential was conducted for MWCNT and TiO₂ nanofluids for all concentrations right after preparation (day 1) of the nanofluid and after 4 weeks. Figure 9 shows the zeta potential setup used. It is Malvern Model having accuracy of ± 0.02 . Figure 10 shows the zeta potential results of these nanofluids on day 1 and after 4 weeks. It can be observed that zeta potential for freshly prepared nanofluid is higher than that of after 4 weeks. The stability of nanofluids decreases over time. However, if the appropriate surfactant is used, the stability lasts longer than usual.

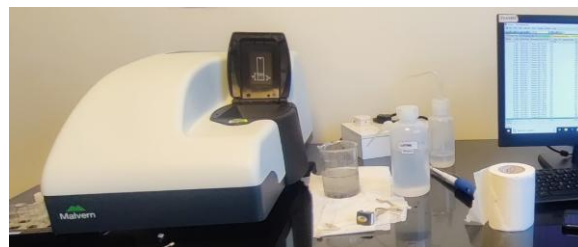


Figure 9: Zeta potential setup.

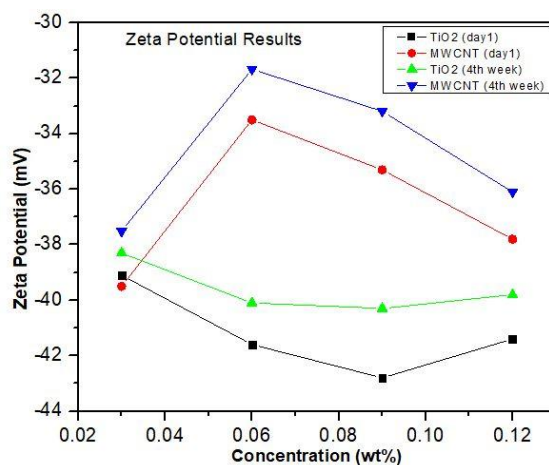


Figure 10: Zeta potential results on day 1 and after the 4th week.

The stability of TiO₂ on day 1 at 0.09 wt% was -42.8 mV and after 4 weeks was -40.3 mV. For MWCNT nanofluid, the stability on day 1 and after 4 weeks at 0.03 wt% was -39.5 mV and -37.51 mV, respectively. The stability of TiO₂ is higher than MWCNT because TiO₂ nanoparticles are hydrophilic

in nature, and they attract water molecules and MWCNT particles are hydrophobic and repel water molecules. However, MWCNT nanofluid was initially prepared by using SDBS as surfactant and the stability was found to be very poor. This forced us to use gum arabic as a surfactant [7]. The stability of TiO_2 at 0.09 wt% and MWCNT at 0.03 wt% decreased by 5.81% and 5.03% over time. Since it is well within the permissible limit, this ensures that these nanofluids can be used even after 4 weeks for heat and mass transfer, energy storage applications. Figure 11(a) and (b) show the MWCNT nanofluid on Day 1 and after 4 weeks, respectively. As observed, the sedimentation is minimal, indicating good stability over time. Similarly, Figures 12(a) and (b) present the TiO_2 nanofluid on Day 1 and after 4 weeks, respectively.

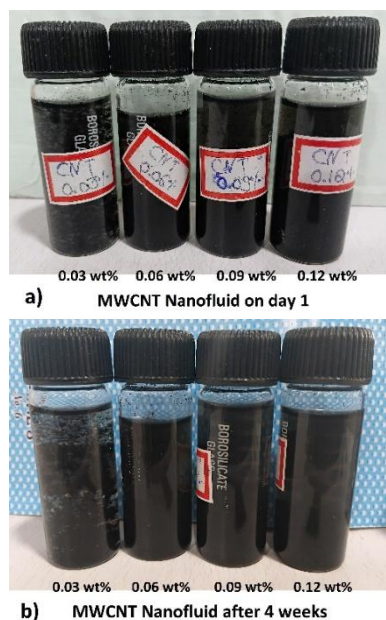


Figure 11: MWCNT nanofluid a) on day 1 and b) after 4 weeks.

Characterization studies of nanofluids were also conducted by UV-vis spectroscopy. It measures the absorbance and transmittance of light within the ultraviolet and visible range as it passes through a sample. For nanofluids, UV-Vis spectroscopy can provide key insights into the interaction between the nanoparticles and the base fluid, allowing researchers to analyze particle concentration, particle size, and the overall dispersion quality. It serves as an indicator of colloidal stability. Nanoparticles suspended in the base fluid can absorb UV-Vis light at characteristic

wavelengths, and changes in absorbance over time may indicate particle agglomeration or sedimentation. Thus, UV-Vis spectroscopy not only aids in understanding the optical performance of nanofluids but also helps monitor their long-term stability, which is critical for practical applications [25]. Figures 13 and 14 show the UV vis result for MWCNT and TiO_2 nanofluids at 0.03, 0.06, 0.09 and 0.12 wt%, respectively. Upon conducting experiments for these nanofluids at given concentrations, it can be seen from the results that the stability of the nanofluids was good.

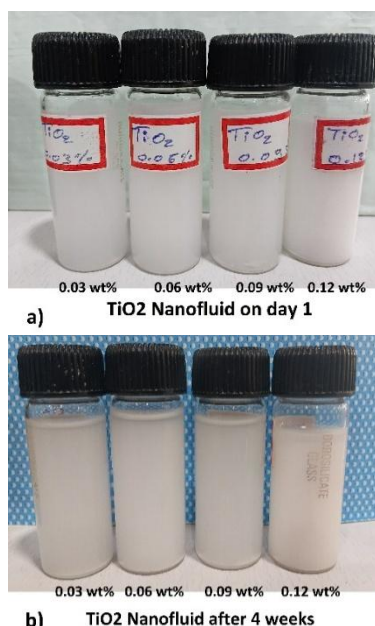


Figure 12: TiO_2 nanofluid a) on day 1 and b) after 4 weeks.

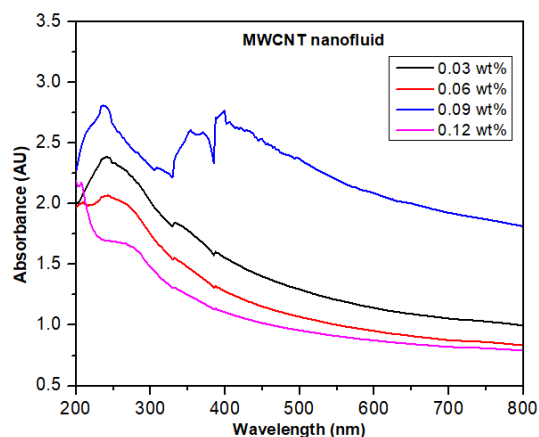


Figure 13: UV-vis spectroscopy for MWCNT nanofluid.

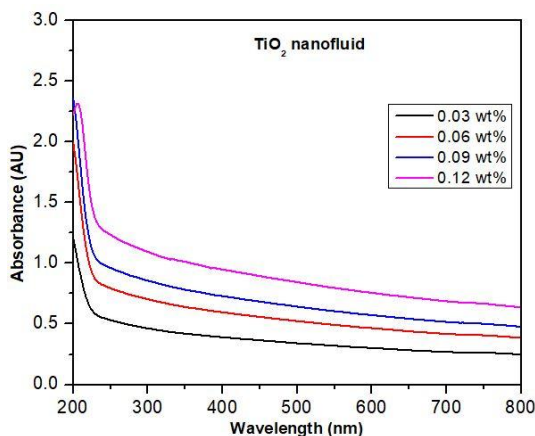


Figure 14: UV-vis spectroscopy for TiO_2 nanofluid.

4 Conclusions

This study demonstrated that the addition of MWCNT and TiO_2 nanoparticles to water significantly enhances CO_2 absorption performance, with each nanofluid showing an optimal concentration for maximum effectiveness. Among the tested samples, MWCNT nanofluids consistently outperformed TiO_2 nanofluids under similar conditions. Stability analysis using Zeta Potential and UV-Vis spectroscopy confirmed good stability of both nanofluids at their respective optimum concentrations, even after four weeks of preparation. These findings suggest that well-prepared nanofluids can serve as effective and stable absorbents for CO_2 capture applications.

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Author Contributions

B.D.: conceptualization, data collection, experimental studies at our lab, methodology, writing of original draft, research design, data analysis, interpretation, submission; D.D.: review and suggestions.

Conflicts of Interest

The authors declare no conflict of interest.

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