Energy Proceedings
Vol 52, 2025
ISSN 2004-2965

From Lab to Industrial Scale: Nano-Enhanced Formulations for Cost-Effective and Efficient Carbon Capture#

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ABSTRACT

Capturing carbon dioxide (CO_2) directly from anthropogenic sources is an essential societal responsibility, particularly in light of the alarming increase in global atmospheric CO_2 levels. Achieving net zero emissions and making our industrial clusters carbon-neutral is challenging and cannot be overcome without the development of large-scale carbon capture technology. Although amine-based absorbents have conventionally served this purpose, their efficacy is hindered by challenges such as low-temperature requirements, energy-intensive regeneration, poor recyclability, susceptibility to corrosion, and oxidative degradation. This study presents a novel nano-enhanced formulation derived from amines, aiming to demonstrate a sustainable CO_2 absorption process that enhances carbon capture performance and reduces regeneration costs for extensive industrial applications. Experimental trials were conducted in an interfacial contact batch reactor at temperatures of 298 K and 318 K using CO_2 with both nanoformulation and conventional amine solutions. The nanoformulation is prepared through a three-step technique involving microgelated nanoparticles and other additives. The SEM, TEM, DLS, and BET characterization were carried out to test nano-enhanced amine solution. Further, thermal analyses such as DSC and TG-DTA were conducted to examine the thermal performance of nanoformulation. Nano-enhanced amines (functionalized amine) exhibit a significant improvement in capture efficiency, approximately 10-12% higher than traditional amine solvents. Additionally, the nanoformulation shows enhanced CO_2 absorption rates compared to traditional MEA (30 wt.%) solutions, and nearly 10 and 55 % enhancement has been reported in absorption rates at 320 and 298 K, respectively. When integrated with other strategies, this approach holds promising potential for carbon capture on industrial scales or directly from the atmosphere.

Keywords: amine, absorption, carbon capture, functionalization, microgelation, nanoparticles.

NONMENCLATURE

Abbreviations	
DEA	*Diethanolamine*
MEA	*Monoethanolamine*
SEM	*Scanning electron microscopy*
DLS	*Dynamic light scattering*
BET	*Brunauer-Emmett-Teller*
DSC	*Differential Scanning Calorimetry*
TGA	*Thermogravimetric Analyzer*
FTIR	Fourier-transform infrared spectroscopy

1. INTRODUCTION

Global warming is a global issue, leading to severe consequences such as rising sea levels, climate change, melting permafrost, species extinctions, and extreme weather events [1–3]. In response to these climatic consequences, countries around the world have sought agreements known as the Paris Climate Accord to reduce carbon emissions and combat climate change[4]. A key objective of this accord is to keep the global temperature rise to within 2°C framework above pre-industrial levels and to significantly decrease carbon dioxide (CO_2) emissions by 2050 [5]. India, as the fourth largest emitter of CO_2 after China, the USA, and the EU, faces significant challenges in achieving its targets of becoming carbon neutral by 2070. This ambitious goal, set under the Paris Climate Accord, necessitates the development and implementation of large-scale CO_2 capture and sequestration technologies[4]. Carbon capture and storage (CCS) technologies are crucial in addressing these challenges[6]. Addressing climatic issues such as global warming requires immediate and effective measures to reduce CO_2 emissions.

This is a paper for the 16th International Conference on Applied Energy (ICAE2024), Sep. 1-5, 2024, Niigata, Japan.

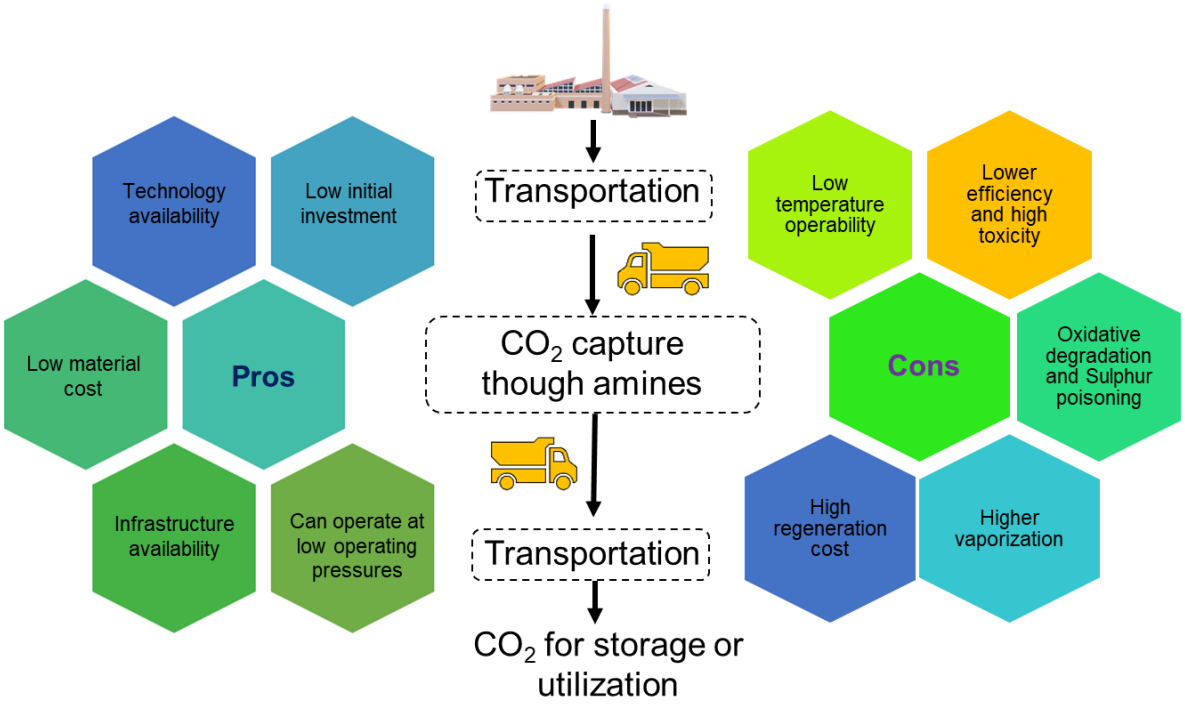

Fig. 1: Advantages and challenges with current amine-based carbon capture technologies.

The primary CCS methods include pre-combustion, oxyfuel combustion, and post-combustion capture [7,8]. Each method has its advantages and own set of challenges:

Pre-combustion capture requires high-pressure conditions to separate CO_2 before combustion, which can be technologically and economically demanding [9]. Oxyfuel combustion involves burning fuel in pure oxygen, producing a flue gas that is more concentrated in CO_2, but it requires substantial energy to produce the necessary high-purity oxygen[9].

Post-combustion capture is the most feasible for retrofitting existing power plants and industrial facilities because it operates at atmospheric pressure and is closer to commercialization[10]. However, it involves significant energy penalties for the capture process. CCS technologies play a crucial role in this effort, with post-combustion capture being particularly relevant for existing infrastructure. Post-combustion CO_2 capture typically employs solvent absorption and solid adsorbent strategies. Solvent absorption, particularly using amines, is beneficial in some aspects but disadvantageous in some other aspects listed in Fig. 1. Continued research and innovation in this field are essential to achieving global climate goals and mitigating the impacts of climate change [11]. Solvent-based methods, particularly those using amine solutions have been extensively used in industrial processes due to their simplicity and cost-effectiveness[12]. Advances in solvent technologies, including the development of amine-functionalized materials/nanoparticles, offer promising avenues for enhancing CO_2 capture efficiency and overcoming existing limitations [13,14]. However, these methods are hindered by issues such as high energy requirements for regenerating the absorbents and problems with corrosion and degradation of materials (**Fig. 1**). Among the solvents used, alkanol amines like monoethanolamine (MEA) and diethanolamine (DEA) are prominent. While these solvents are effective, their efficiency is often constrained by their energy-intensive regeneration process and their tendency to corrode equipment. Capture efficiencies for these solvents generally range between 80-90% [15–18]. The ideal absorbent should have high CO_2 capture capacity, low vapor pressure, fast absorption kinetics, and strong thermal and oxidative degradation resistance [7]. To enhance CCS technologies, research is focusing on developing new solvents and improving existing ones. One promising approach is the functionalization of nanoparticles, such as silica (SiO_2) nanoparticles, to improve CO_2 capture. Functionalizing nanoparticles with amines can increase their effectiveness by providing additional sorption sites for CO_2 absorption, and incorporating these nanoparticles will enhance the overall efficiency of the solvent. The incorporation of amine-functionalized nanoparticles into conventional

amine solutions could address several limitations of current CCS technologies[14]. These nanoparticles can serve as mass transfer agents, improving the rate and efficiency of CO_2 absorption. They also facilitate better interfacial contact area, Brownian motion and micromixing during absorption processes, which can lead to more effective gas-liquid interactions in systems like bubble columns and packed columns [19,20]. Recent research has focused on preparing and characterizing these functionalized nanoparticles. For example, SiO_2 nanoparticles have been modified with amines to enhance their CO_2 adsorption capabilities. The capture performance of these functionalized nanoparticles has been evaluated in this study by dispersing them in MEA solutions with additives and testing their stability, absorption, and desorption characteristics. Characterization techniques such as dynamic light scattering (DLS), thermo-gravimetric analysis (TGA), differential scanning calorimetry (DSC), Fourier-transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM) have been used to analyze the nanoparticles' properties and their interaction with CO_2. These analyses provide insights into the nanoparticles' size, surface morphology, and chemical properties. Gas absorption experiments have been conducted in equilibrium cell (Interfacial contact reactor) at 298 and 320K to assess the performance of the functionalized MEA nanofluids (fMEA) in comparison with conventional MEA solution (30 wt.%). These experiments involve injecting pure CO_2 into the system and measuring parameters such as molar absorption, absorption rate, and volumetric CO_2 loading. The results suggest that the use of amine-functionalized nanoparticles can significantly improve CO_2 capture compared to conventional methods.

2. MATERIALS AND METHODS

2.1 Nanofluid preparation

The preparation of nanoparticles involves a 3-step process beginning with the synthesis and functionalization of the nanoparticles. Initially, TEOS and ethanol are combined and slowly mixed with a solution of ammonia and deionized water in a sol-gel process, stirred for 90 minutes, and then vacuum-dried and calcined to form nanoparticles. These particles are then functionalized with amine groups by suspending them in toluene, adding APTES, and heating the mixture at 325K. After centrifugation and washing, the amine-functionalized nanoparticles are dried. For the final nano-formulation, a mixture of MEA, ethylene glycol, functionalized nanoparticles, SDS, glycine, and water is added in stoichiometric proportion, stirred, and sonicated to create the nanoformulation (fMEA), which is stored in airtight containers for further use in gas absorption experiments.

2.2 Material Characterization

The nanoparticles were characterized using SEM, TEM, FTIR and DLS, with stability measurements conducted through visual and zeta analysis. SEM analysis using a Quanta-400 FEG system revealed that the nanoparticles had a distribution of 100-200 nm. TEM images indicated that most amine-functionalized silica nanoparticles were spherical or quasi-spherical, with signs of amine functionalization on their surfaces (Fig. 2 a, b). The BET analyzer determined the specific surface area and pore volume of these nanoparticles, which were found to be 349.669 m^2/g and 0.655 cm^3/g, respectively—3.5 and 1.5 times higher than that of SiO_2 nanoparticles.

FTIR analysis showed characteristic peaks for SiO_2, including those for Si–O–Si (798 cm^{-1} symmetric stretching; 960 cm^{-1} asymmetric stretching) and Si-OH vibrations, alongside peaks related to C–H and NH bending (1558 cm^{-1}), Si-OH stretching (3750 cm^{-1}) and NH stretching (3500 cm^{-1}) after functionalization with APTS, as depicted in Fig. 2 c.

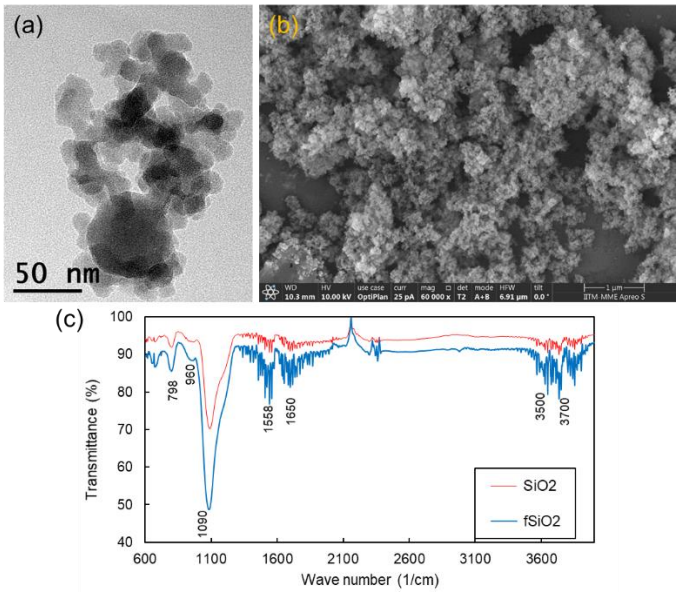

Fig. 2:(a) TEM micrograph of amine-functionalized silica nanoparticles; (b) SEM micrograph of amine-functionalized SiO_2 nanoparticles; (c) FTIR analysis of f-SiO_2 and pristine SiO_2 nanoparticles.

New peaks attributed to CH_2 and N–H vibrations were also identified, confirming successful amine functionalization. Overall, these analyses provide valuable insights into the physical and chemical properties of the nanoparticles and their potential for CO_2 absorption. Further, Dynamic light scattering (DLS) analysis revealed that the average particle size is 170-190 nm, with a negative surface charge indicating good dispersion stability. The average zeta potential of the nanoparticles in the nanofluid is between -50 to -60 mV, which indicates a highly stable dispersion and nanofluid stability.

2.3 Methodology

The experimental setup for the study features a high-pressure reactor (200 ml) made of durable SS-316 stainless steel, capable of withstanding up to 50 MPa and 473K, as shown in Fig. 3. Precision in pressure measurement is achieved with a Delta Ohm HD20V4T piezo-resistive transducer, while accurate temperature control is maintained using a Pt-100 class-A sensor and a temperature-regulated water bath. For CO_2 absorption, a 200 ml autoclave with a stainless steel equilibrium cell is used, where CO_2 is mixed with nanofluid via a magnetic stirrer. The CO_2 absorption process is carried out in an interfacial contact reactor with 40 ml of absorbent, stirred at 300 RPM, and temperature-controlled by an ethylene glycol-water jacket. After purging air and setting the CO_2 pressure, the system reaches an equilibrium pressure that indicates CO_2 saturation. The CO_2-enriched nanofluid is then transferred for analysis. Each experiment is repeated thrice to ensure reproducibility and reliability.

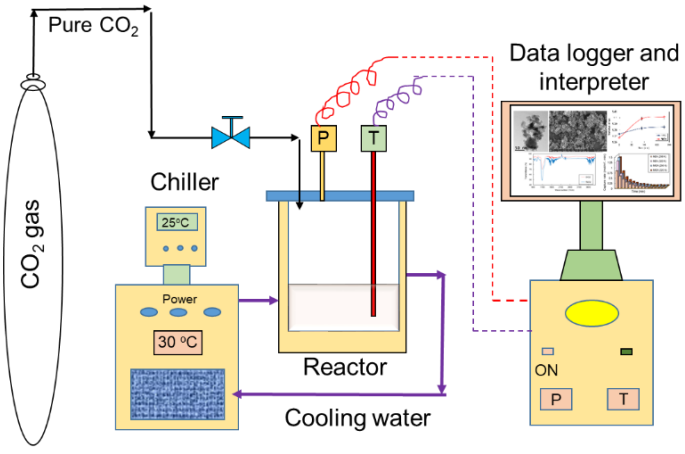

Fig. 3: Experimental setup for the absorption process used in this study.

3. RESULTS

The mole calculations were performed using the Peng-Robinson equation of state, which involved determining the compressibility factor and molar volume of the gas remaining after absorption over different time intervals. The amount absorbed was calculated by subtracting the injected moles from the moles that remained in the gas phase after absorption. After 2.5 hours of reaction, approximately 0.092 and 0.093 moles were absorbed for functionalized MEA (fMEA) at 298 K and 320 K, respectively. In comparison, the absorption for conventional MEA at the same temperatures was around 0.083 and 0.087 moles, as shown in Fig. 4.

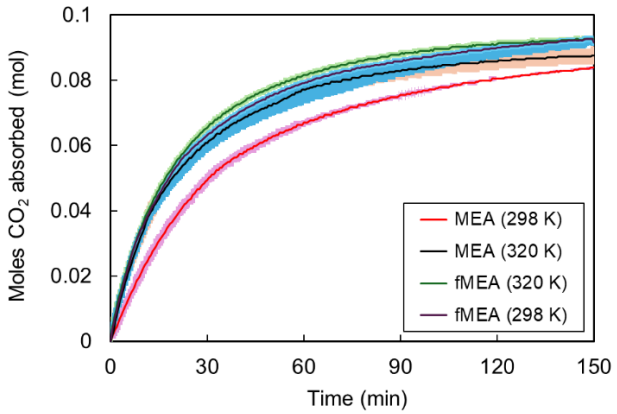

Fig. 4: Total moles of CO_2 absorbed in functionalized MEA solvents and pristine MEA solvent (30 wt. %) at 298 K and 320 K.

The total moles absorbed during the CO_2 absorption process indicate approximately a 10% increase with functionalized nanofluids compared to the conventional MEA solution. To assess the absorption capacity of the solvents, the volumetric CO_2 loading was calculated. At the end of the 2.5-hour period, fMEA exhibited a higher volumetric CO_2 loading compared to the conventional MEA solution. The volumetric CO_2 loadings for the functionalized MEA solution were 2.32 and 2.31 mmol/ml, while for the MEA solution, the values were lower, at 2.19 and 2.09 mmol/ml, as shown in Fig. 5. Notably, the volumetric CO_2 loading for fMEA remained almost the same at both 298 K and 320 K, indicating that the temperature change had a minimal effect on CO_2 loading.

The carbon capture rates were assessed to evaluate the speed at which CO_2 is transferred from the gas phase to the liquid phase. The results indicate that functionalized MEA exhibits higher capture rates compared to conventional MEA solutions. Specifically, the capture rates are highest for fMEA at 298 K, followed by fMEA at 320 K, MEA at 320 K, and MEA at 298 K as

shown in Fig.6. The initial capture rate values for these solvents are 1.38, 1.37, 1.26, and 0.84 mol/m²·min, respectively. The DSC plots of solvents show that the area under the curve is the lowest for functionalized MEA solution, which signifies a lower heat (Energy) requirement during heating and cooling, as depicted in Fig. 7. However, this is a preliminary investigation, and further evidence and analysis are required for heat duty confirmation.

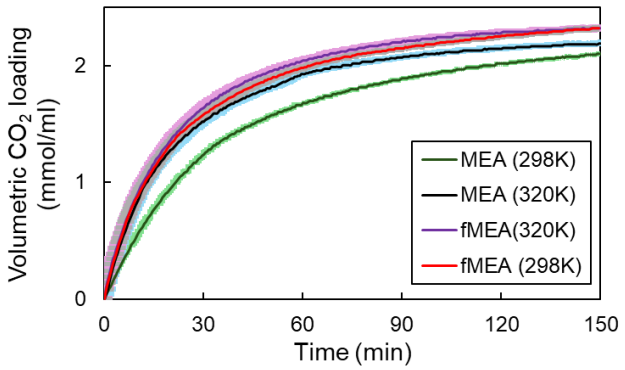

Fig. 5: Volumetric CO_2 loading (mmol/ml) in functionalized MEA solvents and pristine MEA solvent (30 wt. %) at 298 K and 320 K.

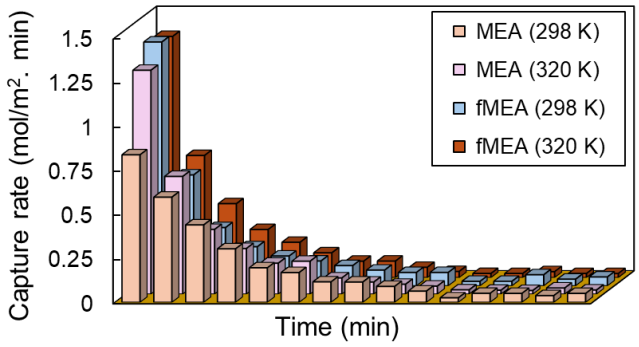

Fig. 6: CO_2 capture rates (mol/m^2. min) in functionalized MEA solvents and pristine MEA solvent (30 wt. %) at 298 K and 320 K.

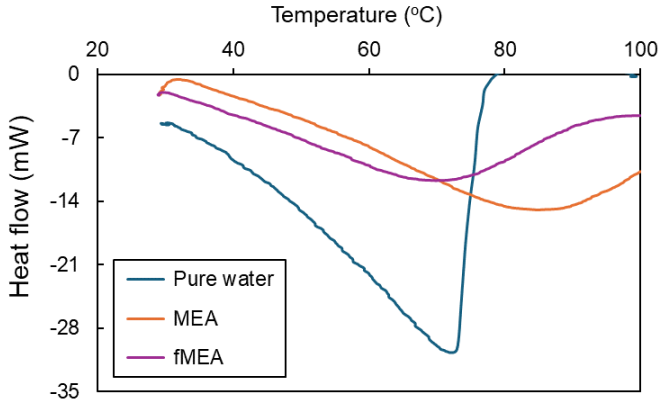

Fig. 7: DSC heat flow analysis of functionalized MEA solvents and pristine MEA solvent (30 wt. %) in comparison with pure water.

The pH and refractive index are important indicators of CO_2 absorption. These properties were measured at 0, 90, and 180 minutes. The refractive index reflects changes in the density of the solvent, which varies as CO_2 dissolves over time. Initially, the refractive index increases significantly during the first 90 minutes as more CO_2 is absorbed, as shown in Fig. 8. However, in the subsequent 90 minutes, the increase in refractive index is less pronounced as the solution approaches saturation with CO_2, leading to reduced mass transfer from the gas to the liquid phase. The pH analysis reveals that the pristine fMEA solution has a lower pH compared to the 30 wt.% MEA solution. The pH values consistently decrease throughout the absorption process due to the dissolution of acidic CO_2 in the basic amine mixture. Additionally, the change in pH is more pronounced during the first 90 minutes than in the following period, as depicted in Fig. 9. However, it is important to note that the change in pH value does not directly represent the number of moles that are dissolved in the solution (Fig. 9).

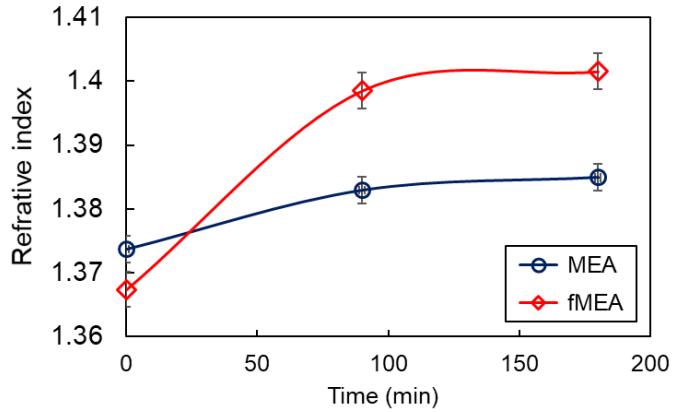

Fig. 8: The change in refractive index value over the timescale of gas absorption experiments.

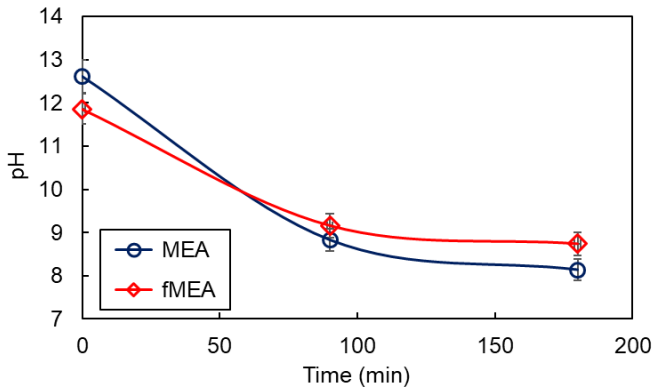

Fig. 9: The change in pH value over the timescale of gas absorption experiments.

4. DISCUSSION

Functionalized nanofluids (fMEA) have demonstrated higher molar absorption, volumetric CO_2 loading, and capture rates in the experiments. The higher carbon capture performance with functionalized MEA nanofluids is owing to the synergistic effect of nanoparticles, surface functionalization, and glycine. The following are the crucial mechanism that comes into play in functionalized nano-enhanced MEA nanofluid.

The synergy of chemicals, additives, and nanoparticles promotes gas absorption in fMEA nanofluid, and the underlying mechanism of absorption enhancement is discussed. Functionalized nanoparticles in nanoformulations significantly enhance micromixing due to Brownian motion and diffusiophoresis, impacting gas absorption processes. Key properties of nanoparticles, such as higher interfacial area and surface characteristics, also play a role. Further, fast-moving nanoparticles break larger gas bubbles into smaller ones, increasing bubble interfacial surface area for gas absorption. Nanoparticles transport these bubbles across the gas-liquid boundary layer, thereby reducing the thickness of the boundary layer (mass transfer barriers) [21]. Further, amine-functionalized nanoparticles facilitate the sorption mechanism and promote both chemisorption and physisorption sites at the nanoparticle surface. The amine groups promote chemisorption, while oxygen molecules act as Lewis acids to chemisorb CO_2. Under higher pressure, CO_2 may be physisorbed onto the carbon chain, enhancing the efficacy of nanoformulation. Overall, the synergistic effects of amines, amine-functionalized nanoparticles, and glycine present a promising solution for effective CO_2 capture and addressing decarburization challenges.

5. CONCLUSIONS

In this study, we evaluated the CO_2 absorption capabilities of a nano-enhanced functionalized MEA nanofluid compared to a conventional 30 wt.% MEA solution. The functionalized nanofluid was synthesized using amine-functionalized SiO_2 nanoparticles, MEA, ethylene glycol, glycine, and water through a three-step preparation process. Characterization of the nanoparticles was performed using SEM, TEM, BET, and FTIR, while the stability and hydrodynamic size of the nanofluids were assessed using DLS. The resulting nanofluid exhibited exceptional dispersion stability. Carbon capture analysis revealed that the functionalized MEA nanofluids achieved approximately 10-12% higher molar capture performance than the conventional MEA solution after 3 hours. Notably, these nanofluids showed significantly enhanced initial capture rates, with nearly a 10% improvement at 298 K and around a 50% improvement at 320 K. Additionally, we assessed other absorption characteristics, such as refractive index and pH, to gain deeper insights into carbon capture processes. Experimental results indicated that the pH of the pristine solvents decreased over time while the refractive index of the solution increased. The outcomes of this research and further advancement in this research domain are significant not only for reducing emissions but also for enabling industries to operate sustainably, comply with regulations, and contribute to global efforts to combat climate change.

ACKNOWLEDGMENT

Yogendra Kumar would like to acknowledge the support from the Prime Minister's Research Fellowship (SB22230926CHPMRF008450). The authors also acknowledge the financial support from Sembcorp Energy INDIA Ltd through CSR grant no: CR23241360CHSEIL008450.

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