Intensification of CO2 absorption and desorption by metallic and non-metallic nanoparticles in bubble columns

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Research Article

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Abstract

In this study, four different metallic and non-metallic nanoparticles including CuO, Fe$_3$O$_4$, ZnO and SiO$_2$ were employed to improve CO$_2$ absorption and desorption in MDEA-based nanouid. CO$_2$ absorption experiment with various nanouids was done in a bubble column reactor at ambient temperature. Also, CO$_2$ stripping experiments for all nanouids were done at 60 and 70 °C. The influence of nanoparticles type, nanoparticle concentration, and the stability of nanoparticles were studied on both CO$_2$ absorption and stripping. The obtained results revealed that Fe$_3$O$_4$ nanoparticles at 0.01 wt.% concentration had the best influence on CO$_2$ absorption and it improved the CO$_2$ loading up to 36%. Also, CO$_2$ stripping experiments for all nanouids were done at 60 and 70 °C. The desorption experiments illustrated that metallic nanoparticles can be more efficient in improving CO$_2$ desorption. In CO$_2$ desorption, the CuO nanoparticles at 0.05 wt.% had higher efficiency, and enhanced CO$_2$ concentration at outlet gas phase up to 44.2 vol.% at 70 °C.

1. Introduction

Fossil fuels are recognized as an important source of energy due to their availability and high energy density. Nonetheless, they play a key part in raising the level of greenhouse gases like CO$_2$ in the atmosphere (Garg et al. 2018). Therefore, mitigating CO$_2$ emission has been the focus of many investigations to control the average temperature of the world (Khalilpour et al. 2017). Although numerous work has been done in introducing new green technologies for providing the required energy of power plants, fossil fuels are still used far more than other types of fuels (Wang et al. 2017). As a result, CO$_2$ capture, utilization and storage seem an undeniable part in reducing CO$_2$ generation caused by fossil fuel production. Accordingly, in CO$_2$ removal from the fossil fuel combustion, CO$_2$ capture is the first step which is categorized into three strategies including post-combustion (PCC), pre-combustion and oxyfuel combustion (Song et al. 2019; Deiana et al. 2017). Of these, the PCC is the most popular strategy which is divided into several typical approaches such as adsorption, membrane, solvent-based absorption-desorption, cryogenic or biological and mineralization (Nanda et al. 2016). It is noticeable that the energy consumption is a crucial factor in offering the best technology for CO$_2$ capture (Liu et al. 2018). Solvent-based absorbent is a well-known technology due to its cost-effectiveness, high performance and high capacity on large scale (Wu et al. 2019; Zhang, Zhang, et al. 2018). On this subject, amine solvents like Monoethanolamine (MEA), Diethanolamine (DEA), Methyl diethanolamine (MDEA), Piperazine (PZ), etc. are recognized as strong chemical absorbents for solvent-based CO$_2$ absorption/desorption. These amines have high absorption capacities and high reaction rates. Nonetheless, there remain some challenges to such absorbents like low vapor pressure, amine solvent degradation and equipment corrosion. However, the high cost of energy consumption in the solvent regeneration section is known as the main problem in the industrial usage of amine solvents because of strong chemical reactions (Akachuku et al. 2019). Therefore, widespread studies have been performed to introduce new approaches for the reduction of energy consumption in amine stripping.
Microwaves (Durán-Jiménez et al. 2020; McGurk et al. 2017; Bougie and Fan 2018; Chronopoulos et al. 2014; Yang et al. 2015; Tsubaki et al. 2020), ultrasonic (Ying et al. 2018; Xing and Feng 2018; Silva et al. 2015; Ma et al. 2016), blended amines (Liu et al. 2017; Shi et al. 2018; Nwaoha et al. 2016; Zhang, Zhang, Yang, et al. 2017) and catalytic promoters (Sahoo et al. 2017; Srisang et al. 2018; Liang et al. 2016; Osei et al. 2017; Zhang, Liu, et al. 2018; Zhang, Zhang, Liu, et al. 2017) are used for improving absorbent solvents regeneration. Although these approaches can be used in gas stripping, they have serious challenges during the enhancement of absorption and desorption processes. For instance, the required energy of microwave/ultrasonic generators is significantly high and catalytic promoters cannot affect the absorption rate, and the blended amines have the same problems as pure amines. Also, based on experimental results in literature studies, it seems that blended amines and catalytic promoters do not have superior impacts in enhancing absorption/desorption efficiency. However, the combination of amine absorbents and effective additives like nanoparticles (NPs) seems an efficient approach to reduce amine solvents problems and regeneration energy costs. NPs can be dispersed in base fluids and lead to changing solvent properties like viscosity, density, mass transfer coefficient, thermal conductivity and heat capacity (Awais et al. 2021). As a result, heat distribution, Brownian motion, mass transfer layering and mass diffusion depth can be improved; therefore, heat and mass transfer can be intensified (Keblinski et al. 2002). Accordingly, applying NPs in the base fluids introduces a variety of beneficial mechanisms to the absorption and desorption sections. The main mechanisms for the improvement of CO₂ absorption are bubble breaking, shuttle effect and hydrodynamic effect. Bubble breaking mechanism states that the CO₂ microbubbles are surrounded by NPs, and NPs with high kinetic energy induce fast dynamic movement to micro-bubbles. High energy of NPs and bubbles can enhance more collision and energy transformation; as a result, more gas-liquid effective contact area is available (Kim et al. 2008; Pineda et al. 2012). Based on the Shuttle effect, the molecules of CO₂ can be adsorbed on the surface of NPs and can be moved from the free gas-liquid interface to depths of liquid bulk (Tinge and Drinkenburg 1992; Linek, Kordač, and Soni 2008; Kluymans et al. 2003). Hydrodynamic effect is another effective mechanism that presents high local turbulence and causes NPs to collide with fluid molecules, leading to the gas-liquid interface being refreshed (Yoon, Chung, and Kang 2014; Kim, Jung, and Kang 2014).

Moreover, the mechanisms of regeneration enhancement in the presence of NPs are summarized in three categories, including activation energy effect, surface effect and thermal conductivity enhancement which affect both mass and heat transfer mechanisms. Because of sticking liquid molecules into NPs with high kinetic energy, the collision between liquid molecules and particles is increased and the average activation energy of particles in solution increases in the presence of NPs (Dutta, Paul, and Chattopadhay 2016). Moreover, the NPs have a positive effect on thermal conductivity enhancement which is shown in different studies (Putnam et al. 2006; Lee et al. 1999; Wang, Xu, and Choi 1999). In other words, NPs have high thermal conductivity compared to the base fluid so that the average thermal conductivity of a solvent can be enhanced by adding NPs to the liquid phase. Therefore, the gas stripping is faster in nanofluids due to fast energy dispersion and rapid temperature enhancement (Fan and Wang 2011). The surface effect is the third mechanism in the improvement of regeneration performance, which causes a change in boiling surface properties such as density of nucleation site, heat transfer area and
roughness (Kim, Jung, and Kang 2013; Kim et al. 2013). Because of the high temperature of the regeneration section, NPs deposition is intensified on the heater surface so that the surface topology of the electrical coil is changed. As a result, a porous layer is created which has more wettability and roughness than the fresh surface of the heater (Wenzel 1949). Moreover, if the NPs cluster size becomes larger than the initial roughness of the surface, the density of nucleation sites on the heater surface can be increased because of more cavities, scratches and pits. (White 2010; Lee, Lee, and Kang 2015). Thus, gas desorption can be improved due to more bubble generation and higher fluid turbulency.

Gas stripping involves the combination of heat and mass transfer mechanisms; therefore, the relationship between heat and mass transfer in improving regeneration process efficiency should be studied in nanofluids (Elhambakhsh and Keshavarz 2021). In this regard, numerous research is performed on the effect of NPs in transformation phenomena. The first study on NPs effects was done by Choi and Eastman in heat transfer mechanism. They employed carbon nanotubes for enhancing the thermal conductivity and reported a 40% improvement in thermal conductivity by nanofluids (Choi and Eastman 1995). Other effective mechanisms on thermal conductivity, including Brownian motion, liquid layering and NPs clustering were investigated by Keblinski et al. (Keblinski et al. 2002). Moreover, Prasher et al. studied the Brownian motion effect in enhancing the thermal conductivity of base fluids (Prasher, Bhattacharya, and Phelan 2006). The diffusion of the fluorescein was examined in the presence of Al₂O₃ NPs by Krishnamurthy et al. They concentrated on heat and mass transfer relationship and revealed that by dispersion of Al₂O₃ NPs, the mass diffusion of fluorescein dye can be increased up to 13 times compared to the pure water as the base fluid (Krishnamurthy et al. 2006).

Although much research is attributed to gas absorption enhancement in presence of NPs, few studies are available on the positive effect of NPs on gas stripping. First, Lee et al. measured the CO₂ absorption and desorption performances by adding SiO₂ and Al₂O₃ NPs to distilled water as a based fluid. CO₂ bubble generation and growth during the regeneration process were monitored; subsequently, they analyzed the cluster size of two NPs with time. They proved that the existence of SiO₂ NPs can improve CO₂ absorption and desorption up to 23.5% and 11.8%, respectively. Moreover, they reported CO₂ absorption enhancement of 23.5% in presence of Al₂O₃ NPs, while the regeneration efficiency was decreased by about 11.2% for Al₂O₃/water (Lee, Lee, and Kang 2015). Soon after, Yu et al. studied CO₂ absorption and desorption in different practical amine solutions, including 30 wt. % MEA, 30 wt. % MDEA and 1.5 mole/L PZ, in presence of SiO₂, TiO₂, Al₂O₃ and CuO NPs. Consequently, they reported the highest regeneration enhancement by adding TiO₂ followed by CuO, SiO₂ and Al₂O₃, respectively. In addition, they showed that Al₂O₃ NPs have more effect on viscosity enhancement of MEA solution than the SiO₂ NPs (Yu et al. 2015). Lee et al. examined the effect of SiO₂ and Al₂O₃ NPs on an absorption/desorption cycle using methanol as a base fluid. They also investigated the regeneration surface properties such as the number of nucleation sites and roughness, as well as their influences on practical features including bubble detachment time and effective surface area of bubbles in the presence of NP. They deduced that changing the heating surface caused by NPs has more effect on CO₂ desorption enhancement than other
agents like thermal conductivity, size and NPs concentration. Moreover, they found that Al$_2$O$_3$ NPs could increase CO$_2$ desorption performance up to 16% compared to pure methanol (Lee et al. 2016). The effects of adding SiO$_2$, TiO$_2$ and Al$_2$O$_3$ NPs on mass and heat transfer mechanisms were studied by Wang et al. They indicated that desorption time can be decreased by 42% by using 0.1 wt.% of TiO$_2$ (Wang et al. 2016).

As a result, it can be deduced that the NPs are effective additives for enhancing CO$_2$ uptake and solvent regeneration. Moreover, among various types of NPs, magnetic nanoparticles can be more appropriate due to their widespread advantages, including low toxicity, large surface-to-volume ratio, superparamagnetic properties and reutilization (Schaetz, Hager, and Reiser 2009; Esmaeilpour et al. 2017; Peyravi, Keshavarz, and Mowla 2015). In addition to these advantages, magnetic NPs can be simply recovered from the nanouids by an external magnetic field (Elhambakhsh and Keshavarz 2020). Moreover, because of the metallic and magnetic properties of magnetic NPs, they have a positive influence on the gas stripping via the improvement of heat transfer process.

Although magnetic NPs are used in several studies of CO$_2$ absorption, they are not employed for solvent regeneration enhancement in literature research. In this work, Fe$_3$O$_4$ NPs in combination with methyl diethanolamine (MDEA, as base fluid) were used in the CO$_2$ absorption/desorption process and the result was compared with different kinds of NPs such as SiO$_2$, ZnO and CuO. As far as we are aware, this is the first study of applying magnetic NPs for CO$_2$ desorption. All mentioned NPs were employed at various concentrations, and regeneration tests were done at different temperatures. CO$_2$ loading at the end of each process (absorption and stripping) in the liquid phase and flow rate and CO$_2$ concentration in the outlet gas stream were measured and examined. Ultimately, the impacts of different operational conditions including the type of nanoparticles, nanoparticles concentration, and the stability of nanoparticles on CO$_2$ absorption/desorption were studied and discussed.

2. Experimental And Methods

2.1. Nanofluid preparation

In the first step, 10 wt.% solution of methyl diethanolamine (MDEA), as base fluid, was provided in 1700 ml by combination of 164 ml MDEA (99% purity) and 1536 ml double distilled water. In this study, the nanofluid was created by adding different weight of NPs including SiO$_2$, ZnO, CuO and Fe$_3$O$_4$, with 99% purity. So far, for all nanoparticles, 0.170, 0.851 and 1.702 gr NPs were added to base fluid to achieve nanofluid with 0.01%wt, 0.05%wt and 0.1%wt NPs concentrations, respectively. Next, a hand-made mechanical stirrer was used to stabilize NPs in the base solution in 30 min steps. Moreover, C-Tab surfactant with 1:1 weight ratio (NPs to surfactant) was employed to promote NPs dispersion. In addition, ultrasonic irradiation (model Tomy, UD-201, Japan) was applied on nano fluid for 20 min to avoid NPs agglomeration.
2.2. Experimental setup

Figure 1 shows the schematic of the experimental semi-batch setup that was used in CO\textsubscript{2} absorption and stripping tests. The main part of this apparatus was a plexiglass column with a 3000 ml effective volume. An airstone was installed on the bottom section of the column to introduce a bubble-shaped inlet gas stream (pure CO\textsubscript{2} in absorption tests or purged air in regeneration tests) in the column, that can deform or grow in solvent media. These bubbles can deform or grow in solvent media. For analysis of CO\textsubscript{2} concentration in the liquid phase, a tube sampler was attached to the bottom of the device. Because a described experimental setup was used in absorption and regeneration tests, an electrical heating element was installed in the center of the column to supply the required temperature for CO\textsubscript{2} desorption. It is noticeable that 3–5 min was considered as the delay time of the electrical coil to achieve the desired temperature. Moreover, a control system, including a thermostat with a precision of 0.1 °C, was employed to hold fluid in the setpoint temperature during the regeneration process. In this regard, the thermostat was fixed on the bottom platform at a desirable distance from the electrical coil. Herein, a condenser and gas-liquid separator were placed on the top of the column to remove the moisture in the outlet gas phase. In addition, a gas flow meter and CO\textsubscript{2} analyzer were installed following the gas-liquid separator to analyze the gas phase.

2.3. Experimental procedure

The described semi batch apparatus was used in absorption tests at ambient pressure and 20 °C. For this purpose, nanouids were prepared in 1700 ml with different concentration of NPs as explained. Then, pure CO\textsubscript{2} (purity >> 99%) was introduced to fresh nano-solvents for 45 min as bubbles for CO\textsubscript{2} absorption. It is noticeable that, the inlet CO\textsubscript{2} flow rate should be set at appropriate value to achieve the highest CO\textsubscript{2} concentration in liquid phase and to avoid gas channeling. Therefore, the gas flow meter was fixed at 175 ml/min for inlet CO\textsubscript{2} flow rate. Because the CO\textsubscript{2} absorption performance was expressed as CO\textsubscript{2} loading (mole of CO\textsubscript{2} to mole of amine), 20 ml liquid sample was collected at the end of each experiment to determine the CO\textsubscript{2} content in nano solution after 45 min. Finally, CO\textsubscript{2} loading in nano fluid was determined by precipitate method and it was iterated for three times to avoid uncertainty in experimental results.

In this research, another essential experiment was solvent regeneration test which was done for 72 min. In this time, the thermal coil was fixed at set point temperatures as 60 and 70 °C and air compressor was replaced by CO\textsubscript{2} cylinder to offer purge air in vessel with 200 ml/min flow rate. In these experiments, outlet gas flow rate and its CO\textsubscript{2} content were considered as major index to investigate the performance of NPs in regeneration process. Therefore, the flow rate and CO\textsubscript{2} content of gas phase in the top stream of column was recorded to analyze the regeneration performance. Moreover, the initial and final CO\textsubscript{2} loading in regeneration section should be compared, therefore another liquid sample was assembled, after the regeneration time. Moreover, each of the experiments was repeated three times to be sure of the accuracy of the results.
2.4. CO₂ loading

The mole of CO₂ in liquid phase per mole of amine is introduced as CO₂ loading that is an important index in gas absorption and stripping studies (Salvinder et al. 2019). Higher CO₂ loading in absorption process shows better condition for CO₂ capture and high performance of process. Moreover, the low CO₂ loading at the end of regeneration process was expressed as more desirable operational condition to access more CO₂ stripping.

The CO₂ loading was determined by precipitate approach, that was based on weighting BaCO₃ sediment (Santos 2013). For this purpose, 20 ml sample of liquid phase was collected and 1 M NaOH solution was added in excess to liquid sample in order to convert CO₂ molecules to nonvolatile component. Then, 1 M BaCl₂.2H₂O solution was used in excess as previous step to create BaCO₃ precipitate. Finally, the sample was stirred to achieve stable precipitate, and then, the precipitate was filtered, dried and weighted.

The CO₂ mole in amine solution was calculated by the following correlation:

\[ n_{CO₂} = \frac{m_{pre}}{MW_{BaCO₃}} \]

1

Where \( m_{pre} \) is mass of precipitate as gr and \( MW_{BaCO₃} \) is the BaCO₃ molecular weight. Moreover, the amine mole was determined by the following equation:

\[ w_{amine} = w_{sample} \times C \]

2

\[ n_{amine} = \frac{w_{amine}}{MW_{amine}} \]

3

Where \( w_{sample} \), \( C \) and \( MW_{amine} \) are defined as weight of sample, amine solution concentration and amine molecular weight, respectively. So far, CO₂ loading is specified as the ratio of \( n_{CO₂} \) to \( n_{amine} \):

\[ CO₂\text{loading} = \frac{n_{CO₂}}{n_{amine}} \]

3

3. Results And Discussion

3.1. Nano-Solvent stability
NPs tendency of agglomeration and sedimentation was studied by zeta potential analysis. Accordingly, the absolute zeta potential of high stable nanofluids is more than 60 mV and the absolute zeta potential between 30 and 60 mV shows an acceptable stability for the nanofluids. It is noticeable that the absolute zeta potentials for medium and weak stabilities are related to 20 mV- 30 mV and 0 mV – 20 mV, respectively. In this work, Horiba SZ-100 dynamic light scattering device was employed to investigate the stability of nanofluids. Thus, NPs were dispersed in 10 wt.% MDEA solution by applying ultrasonic agitator (model Tomy, UD-201, Japan). The results of absolute zeta potential for different nanofluids were reported in Table 1.

### Table 1
Zeta potential values for various NP concentrations.

<table>
<thead>
<tr>
<th>Nanofluid</th>
<th>Absolute zeta potential (mV)</th>
<th>Stability</th>
<th>Nanofluid</th>
<th>Absolute zeta potential (mV)</th>
<th>Stability</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$ (0.01 wt.%)</td>
<td>32.5</td>
<td>Stable</td>
<td>Fe$_3$O$_4$ (0.01 wt.%)</td>
<td>44.5</td>
<td>Stable</td>
</tr>
<tr>
<td>SiO$_2$ (0.05 wt.%)</td>
<td>34</td>
<td>Stable</td>
<td>Fe$_3$O$_4$ (0.05 wt.%)</td>
<td>40.9</td>
<td>Stable</td>
</tr>
<tr>
<td>SiO$_2$ (0.1 wt.%)</td>
<td>30.5</td>
<td>Stable</td>
<td>Fe$_3$O$_4$ (0.1 wt.%)</td>
<td>19.7</td>
<td>Unstable</td>
</tr>
<tr>
<td>ZnO (0.01 wt.%)</td>
<td>42.5</td>
<td>Stable</td>
<td>CuO (0.01 wt.%)</td>
<td>34.2</td>
<td>Stable</td>
</tr>
<tr>
<td>ZnO (0.05 wt.%)</td>
<td>44.1</td>
<td>Stable</td>
<td>CuO (0.05 wt.%)</td>
<td>38.9</td>
<td>Stable</td>
</tr>
<tr>
<td>ZnO (0.1 wt.%)</td>
<td>49.2</td>
<td>Stable</td>
<td>CuO (0.1 wt.%)</td>
<td>20</td>
<td>Unstable</td>
</tr>
</tbody>
</table>

### Table 2 Specifications of employed NPs.

<table>
<thead>
<tr>
<th>Nanoparticles</th>
<th>Color</th>
<th>Morphology</th>
<th>Particle size</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_3$O$_4$</td>
<td>Black</td>
<td>Spherical</td>
<td>9–12 nm</td>
</tr>
<tr>
<td>CuO</td>
<td>Black</td>
<td>Spherical</td>
<td>10–12 nm</td>
</tr>
<tr>
<td>ZnO</td>
<td>White</td>
<td>Spherical</td>
<td>40≥</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>White</td>
<td>Spherical</td>
<td>15–21 nm</td>
</tr>
</tbody>
</table>

3.2. Effect of nanoparticle type on CO$_2$ absorption enhancement
Figure 2 shows the CO₂ absorption ability as CO₂ loading for the bare MDEA solution and MDEA based nanofluids of SiO₂, ZnO, Fe₃O₄ and CuO at 0.01 wt.%, 0.05 wt.% and 0.1 wt.% concentrations and 289 K. The experimental results revealed that all nano-solvents resulted in a higher CO₂ absorption compared to the base fluid. As shown, Fe₃O₄ nanofluid has the highest CO₂ loading at concentration 0.01 wt.% and the CO₂ loading of Fe₃O₄ nanofluid is decreased with raising the amount of NPs. The CO₂ loading for Fe₃O₄ nanofluid is enhanced to 8.2%, 18.4% and 32.6% at the concentrations of 0.1, 0.05 and 0.01 wt.%, respectively.

The CO₂ loading for CuO nanofluid is enhanced up to 23, 26 and 8% at concentrations of 0.01, 0.05 and 0.1 wt.%, respectively, indicating that CuO nanofluid has the best performance at the optimal concentration of 0.05 wt.%. Also, the high efficiency of ZnO was observed at 0.1 wt.% concentration as 0.61 CO₂ loading. The ZnO nanofluids with 0.05 wt.% and 0.01 wt.% concentration have 0.57 and 0.54 CO₂ loading, respectively. In addition, SiO₂ NPs could promote CO₂ loading up to 9% at 0.05 wt.%. The obtained results are justified by the result of zeta potential analysis, indicating the stability of nanofluids. The stability of nanofluids are considered as a significant factor in raising CO₂ absorption. Thus, absolute zeta potential is used to explain the ability of various NPs and the results are summarized in Table 1–2. It is noticeable that higher absolute zeta potential indicates higher stability and lower tendency to aggregation at nanofluids (Nabipour, Keshavarz, and Raeissi 2017). Therefore, more active surface at stable nanofluids lead to better performance for CO₂ uptake (Elhambakhsh et al. 2020). For instance, a high absorption performance of Fe₃O₄ nanofluid at concentration 0.01 wt.% can be attributed to its high stability (Table 1) as well as its low particle size (Table 2).

### 3.3. Solvent regeneration

Unlike the gas absorption, gas stripping is related to both mass and heat transfer mechanism. Thus, some thermal properties such as thermal conductivity and thermal diffusivity of nanofluid can be recognized as important properties in improving gas desorption as well as mass transfer properties. As a result, this parameter should be examined for each one of the NPs, to determine best candidate for CO₂ stripping.

The outlet gas flow rate and its CO₂ content for all mentioned nanofluids is shown in Figs. 3, 4, 5 and 6. It is noticeable that each one of the experiments was done three times to determine error bar of graphs. However, the error bars are demonstrated only for CuO nano-fluid to avoid graphs cluttering.

### 3.3.1. Effect of nanoparticles concentration on regeneration process

According to experimental results, the effects of all nanofluids in enhancing CO₂ stripping are shown in Figs. 3–6. Figure 3a-b and Fig. 3c-d show the amount of CO₂ concentration in the outlet stream and outlet gas flow rate, respectively, for CuO nano-solvent over a period of 72 min at the regeneration
temperature of 60 and 70 °C. Although the CuO resulted in a low impact on CO₂ absorption, it has a significant impact on regeneration process so that applying CuO led the desorption capability of MDEA solution to increase up to 93% at the NPs concentration of 0.05wt.% and 70 °C.

The NPs have two essential effects on heat and mass transfer, enhancing the CO₂ stripping by nanofluids. In the view of mass transfer, the NPs can provide a higher mass transfer coefficient in the base fluid due to applying various effective mechanisms like Brownian motion, grazing effect and bubble breaking. The details of these mechanisms were mentioned in our previous work (Elhambakhsh et al. 2021). Further, the NPs can improve the regeneration by changing the heating surface properties and increasing the average thermal conductivity of solutions. However, NPs may cause different behaviors in improving the heat and mass transfer of solutions. Although the thermal conductivity of nanofluids can be increased by raising the NPs concentration, several properties such as nano-solvent stability, viscosity and density might have not the same behavior and can even lead to negative effects on mass transfer when the NPs concentration is more than a certain value.

As can be seen, the CO₂ stripping amount for all nano-solvents has a sharp trend at the first 10 min. This behavior occurs for all nanofluids and MDEA solution, however nanofluids had a higher peak compared to the base fluid that is attributed to physical absorption of CO₂ micro molecules (Kars, Best, and Drinkenburg 1979; Golkhar, Keshavarz, and Mowla 2013).

The proportion of CO₂ desorption is related to chemical absorption by the liquid phase and physical adsorption on the surface of NPs. And, the amount CO₂ desorption in the first 10 min after the start regeneration is, mainly, related to the desorption of the adsorbed CO₂. However, after this time, the desorption depends on the chemical bonds between the liquid phase and CO₂ (Tumuluri et al. 2017).

Figure 4a-d demonstrates the results of the same experiment for Fe₃O₄ nanofluid. As shown, the CO₂ desorption is in the highest amount at 0.05 wt.% Fe₃O₄ nanofluid and the lower CO₂ desorption is obtained at 0.1 wt.%. This lower desorption value can be due to the low amount of absolute zeta potential at 0.1 wt%, which reduces the performance of Fe₃O₄ nanofluid (Table 1).

Similar results are also acquired for ZnO and SiO₂ nanofluids and the 0.05 wt.% is introduced as an optimal concentration for these two nano-solvents. The results for these nanofluids are depicted in Figs. 5-6.

### 3.3.2. Effect of nanoparticles Types on CO₂ stripping at optimum concentration

Figures 7–8 show the final results of CO₂ desorption after 72 min for the employed nanofluids at optimum concentration. As can be seen, the final CO₂ loadings of metallic NPs of CuO and Fe₃O₄ at optimum concentration (0.05 wt.%) are much lower than non-metallic ones, indicating the metallic NPs have been more effective than other NPs, during the regeneration process. Furthermore, the CuO nano
fluid offers higher performance than the $\text{Fe}_3\text{O}_4$ nano solution at optimum concentration. Because of the higher thermal conductivity, CuO NPs have the highest impact on the improvement of nanofluid thermal diffusivity. This leads to more CO$_2$ being released from the nanofluid during the similar regeneration time. As another metallic nanofluid, Fe$_3$O$_4$ is the second successful nano-solvent in CO$_2$ desorption, followed by ZnO and SiO$_2$.

The surface effect is recognized as an effective parameter in enhancing gas stripping (Kwark et al. 2010). The NPs deposition leads to the creation of a porous layer on the heating surface during the regeneration that changes the wettability and roughness of electrical coil that can increase heat transfer resistance. As a result, the thermal properties of NPs have remarkable influence on the porous layer thermal resistance. Therefore, the NPs with higher thermal conductivity can reduce the thermal resistance of the porous layer.

It is noticeable that CuO and Fe$_3$O$_4$ nanofluids are still active at the end of regeneration process. Nonetheless, ZnO and SiO$_2$ NPs have lower impacts and their performances are very low. Therefore, CuO and Fe$_3$O$_4$ nano fluids are good candidates compared to other NPs due to more activity during regeneration time as well as favorable metallic properties like high thermal conductivity. The details of final CO$_2$ loading are stated in Supplementary information section (Table S1).

4. Conclusions

In this investigation, the metallic (CuO and Fe$_3$O$_4$) and non-metallic NPs were employed for the intensification of CO$_2$ absorption and subsequently the effects of the NPs on enhancing CO$_2$ stripping were studied. Based on the obtained results, all nano fluids revealed higher impacts in improving gas absorption and desorption than the bare MDEA solution. In CO$_2$ absorption, the highest performance was attributed to Fe$_3$O$_4$ NPs. And, the Fe$_3$O$_4$ NPs at 0.01 wt.% concentration increased CO$_2$ loading to 35.7% at the end of absorption time. In addition, SiO$_2$ NPs had lower influence on CO$_2$ absorption and it improved the CO$_2$ loading just up to 8.9% at its best concentration. Also, the NPs were applied to improve CO$_2$ desertion at various concentrations. The results demonstrated the more capability of CuO and Fe$_3$O$_4$ nanofluids in raising CO$_2$ stripping and they enhanced CO$_2$ content at outlet gas phase up to 0.442 and 0.303 volume fraction, respectively, as a result of higher thermal conductivity and more energy diffusivity as well as lower average NPs size.

Declarations

1. Ethical Approval: Not applicable.

2. Consent to Participate: Not applicable.

3. Consent to Publish: Not applicable.

4. Authors Contributions:
• **Fariba Zarei**: Methodology, Data curation, Investigation, Resources, and Writing - review & editing.
• **Peyman Keshavarz**: Conceptualization, Visualization, Supervision, Project administration, and Funding acquisition.

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6. **Competing Interests**: The authors declare that they have no competing interests.

7. **Availability of data and materials**: All data generated or analysed during this study are included in this published article (and its supplementary information files).

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Figures
**Figure 1**

Figure 2

Effect of nanoparticles type on CO$_2$ loading at the end of 45 min absorption time.
Figure 3

Effect of CuO nano fluids on CO$_2$ desorption during regeneration process with 220 ml/min purge air. a) based on outlet CO$_2$ volume fraction at 60 °C. b) based on outlet CO$_2$ volume fraction at 70 °C. c) based on output gas flow rate at 60 °C. d) based on output gas flow rate at 70 °C.
Figure 4

Effect of Fe$_3$O$_4$ nano fluids on CO$_2$ desorption during regeneration process with 220 ml/min purge air. a) based on outlet CO$_2$ volume fraction at 60 °C. b) based on outlet CO$_2$ volume fraction at 70 °C. c) based on output gas flow rate at 60 °C. d) based on output gas flow rate at 70 °C.
Figure 5

Effect of ZnO nano fluids on CO₂ desorption during regeneration process with 220 ml/min purge air. a) based on outlet CO₂ volume fraction at 60 °C. b) based on outlet CO₂ volume fraction at 70 °C. c) based on output gas flow rate at 60 °C. d) based on output gas flow rate at 70 °C.
**Figure 6**

Effect of SiO$_2$ nano fluids on CO$_2$ desorption during regeneration process with 220 ml/min purge air. **a**) based on outlet CO$_2$ volume fraction at 60 °C. **b**) based on outlet CO$_2$ volume fraction at 70 °C. **c**) based on output gas flow rate at 60 °C. **d**) based on output gas flow rate at 70 °C.
Figure 7

Effect of different nano fluids on the final CO$_2$ loading at the end of 72 min regeneration process with different temperature.
Figure 8

Effect of different nanoparticles at optimum concentrations on CO$_2$ desorption at 70 $^\circ$C regeneration temperature and 220 ml/min purge air. a) based on outlet CO$_2$ volume fraction. b) based on output gas flow rate.
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