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Improvement of CO_2 Absorption/Desorption Rate Using New Nano-Fluid

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ABSTRACT

Increasing the serious impact of the emissions of carbon dioxide (CO_2) on the warming of globe and change of climate make this issue is one of the most important issues facing the world that needs to be resolved urgently. Several techniques have been used to control CO_2 emissions. One of the methods that achieved good results was the chemical absorption technique using absorption solutions. Recently, nano solutions have been used. This action has received attention. However, further studies are needed to enhance the absorption/desorption of nano fluids and reduce the energy requirements for the regeneration process. In this study, the nanoparticle suspended in blend of monoethanolamine and triethanolamine are utilized as a new solvent. Ultrasonic was used to obtain good suspension of the nanoparticle into the base fluid and also to ensure high stability. The results showed that the CO_2 absorption using the Nano fluid is enhanced by ~28% for Al_2O_3, 19% for Fe_2O_3 and 15% for SiO_2 compared to that with using the base fluid alone. In addition, the rate of CO_2 desorption was increased by 47%, 28%, and 22% using the Nano fluids of Fe_2O_3, SiO_2, and Al_2O_3, respectively, compared with the desorption rate of the base fluid without nanoparticles.

1. INTRODUCTION

The greenhouse gases are mainly consist of Carbon dioxide (CO_2) compared with the concentration of other gases. The concentration of CO_2 in the air is growing by reason of the industrial revolution. Therefore, the significant danger to the climatic is increasing [1, 2]. Several technologies were applied to capture CO_2 effectively such as: physical and chemical absorption, spread through organic and inorganic membranes, adsorption and cryogenic process [1-3]. Commercially, the most method used to capture CO_2 is chemical absorption using alkanolamines aqueous solutions [3, 4]. Capturing CO_2 by alkanolamines requires various alkanolamines aqueous solutions like monoethanolamine (MEA), triethanolamine (TEA), Diethanolamine (DEA) or 2-amino-2-methyl-1-propanol (AMP). There are many classes of alkanolamines with different physical and chemical properties. Generally, Primary (MEA) and secondary amines (DEA), have a high reactivity with CO_2 and consume high energy for regeneration. However, Tertiary amines (TEA) have slow reaction with CO_2, high loading capacity, and low regeneration energy consumption. Moreover, sterically hindered amine (AMP), these amines are similar to tertiary amine in (loading capacity). The most common amine used in the CO_2 absorption process was 5M of MEA aqueous solution due to a good reaction kinetic with CO_2, low cost and easy to be used. However, the high energy required for regenerating the solvent, the high degradation property and the corrosive nature of solvent were considered as the main difficulties that facing with using MEA [2, 5]. Therefore, the discovery of new solvents better than MEA is the most important challenge facing the post-combustion capture technology. Accordingly, the approaching of the optimum solvent (the high ability of absorption, and low energy for regeneration) needs to evaluate many solvents to find the ideal solvent. Consequently, researchers concentrated on the improvement of new solvents. They discovered that the blending of two or more types of amines enriched the properties of a single amine [2, 6-9]. As well, they found that the blend of AMP with MEA has an absorption capacity higher than MEA alone and that is because of the influence of primary amine (have high CO_2 kinetic reaction) and sterically hindered amine (have high absorption capacity of CO_2) [9, 10]. Therefore, the blending of amines could be lessening the weaknesses of commonly used solvents. In Addition, recent studies reported that the addition of nano particles to the solvent increase both gas absorption and desorption rate [5, 8]. Nano fluids can be prepared by suspending particles with diameter of 100 nm or less in a suitable fluid [7]. So far, the effect of nanoparticles on the mass transfer in gas-liquid systems needs more investigation [5]. Therefore, the aim of this work was to study the improvement of CO_2 absorption/desorption property of bi blend alkanolamine with nanoparticles. Altered nanoparticles of 80 nm particles sizes with different concentration, vol. %, were also studied. In addition, the Essential relationship between particle concentration and absorption/desorption was discussed. Finally, the effect of dispersant was reduced by the dispersion technique using ultrasonic.

2. MATERIALS AND EXPERIMENTAL METHODS

2.1 Chemicals and equipment

MEA (99%), Hydrochloric acid (HCl), MEA (98%), TEA (99%) and nanoparticles with 80nm in diameter with purity of (99.9%) (Silicon oxide (SiO_2), Iron oxide (Fe_2O_3) and Aluminum oxide (Al_2O_3)) (Acquired from sigma Aldrich, India). All materials used without additional purification. Gas cylinders of N_2 (99.99%) and the CO_2 (99.99%) used for the flue gas simulation. The specifications of the used equipment were: Analytical balance, OHAUS /U.S.A, readability 0.0001 g, Glass ware, Glassco /India, Hot plate stirrer, Labtech / Korea, 60 – rpm, Max. temperature 380℃, Thermometer, Germany, Mercury (0–200)℃, CO_2 analyzer, Atmocheck double O_2/CO_2/ U.S.A, Range (0.00 – 100)% and Flow meters, Flowtech /U.S.A, N_2 (25-250) ml/min, CO_2 (25-250) ml/min), Ultrasonic,max temperature 60℃, minimum fluid level 80 mm.

3. EXPERIMENTAL SYSTEM

3.1 Preparation of nano fluid

The Nano fluids used in the experiments were prepared following Figure 1. At first the base solvent prepared by blending MEA (monoethanolamine) with TEA (triethanolamine) by 3/3 molar ratio and stirred for 15 minutes at room temperature to get a homogeneous solution. Then, the nanoparticles were sprinkled into the (3M MEA/3M TEA) using ultrasonic to confirm the well dispersal of nanoparticles in the based solvent. Then, the steadiness of the nano fluid was tested by visual observation in the nano fluid container after 24 hours. Figure 2 showed the stability of BBAAS with SiO_2, Al_2O_3, and Fe_2O_3.

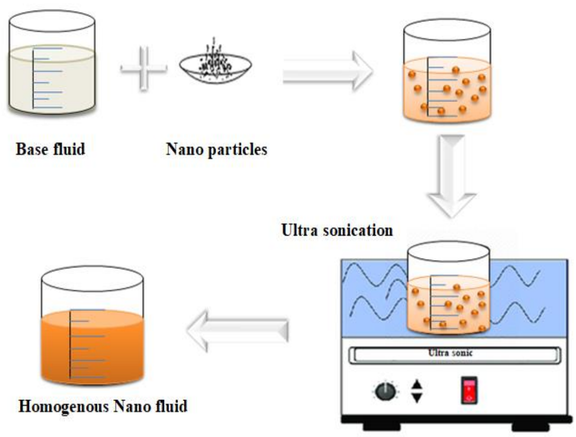
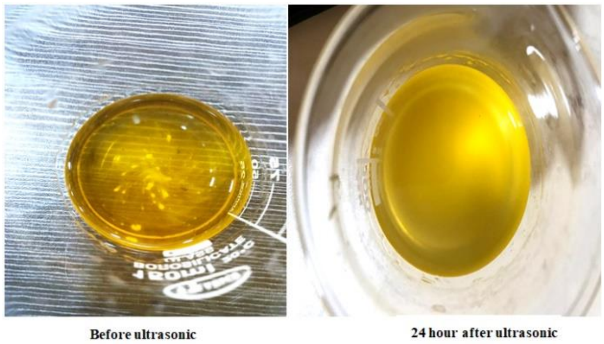


Figure 1. Nano fluid preparation steps

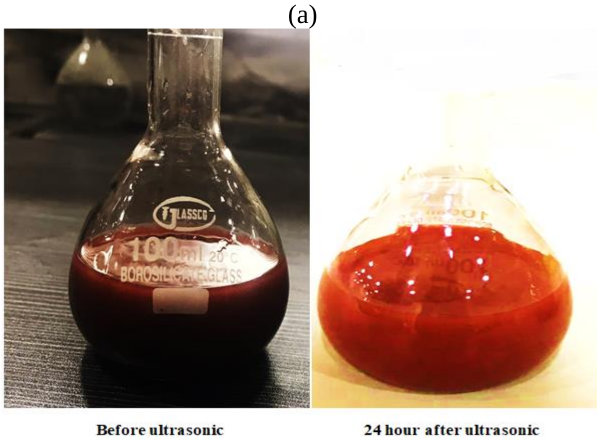
3.2 CO_2 absorption/desorption apparatus and methods

The CO_2 absorption experiments were conducted in a 100 ml glass reactor as presented in Figure 3. The CO_2 / N_2 gas streams were mixed to a chosen CO_2% (15 vol. %) by adjusting their flow meters accurately. Then, the gas mixture contacted with the prepared nano fluid through the absorption cell. Moreover, the absorption/desorption examination of all scanned the nano fluid were occurred at identical CO_2 partial pressure, gas flow rates and temperature to ensure accurate estimation. Then, the gas mixture at 200 L/hr passes through the nano fluid using absorption cell. The exit gas from the absorption cell was analyzed using CO_2 analyzer every one minute until the nano fluid becomes saturated with CO_2. After that, the effect the presence of nanoparticles on the absorption rate of CO_2 was calculated.

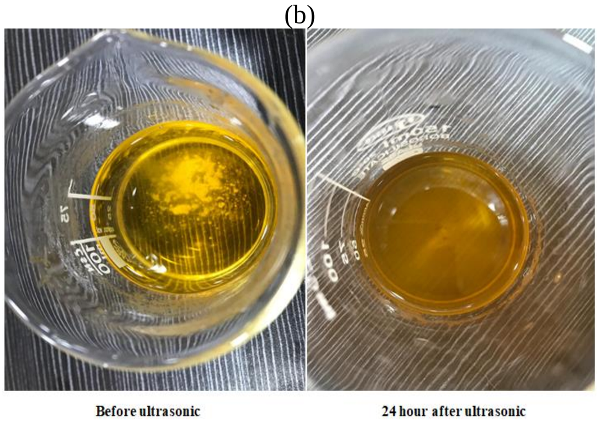
Furthermore, the saturated nano fluid tested by desorption process as applied on following our previous work [4]. Figure 4 describes schematically the drawing of the desorption process. The desorption apparatus consists of heating plate to provide the necessary heat to the insulated oil bath that heating the nano fluid to the preferred temperature. The 40ml of saturated nano fluid was placed into the 100 ml desorption cell. Then, the desorption cell dipped into the oil bath till the neck to avoid heat losses. A condenser was used to reduce the nano fluid losses by water flow through at room temperature. A thermometer, Germany, Mercury (0 – 200)℃ placed in to the both desorption cell/oil bath to approve the required temperature.



(a)



(b)



(c)

Figure 2. The stability of BBAAS with (a) SiO_2 (b) Fe_2O_3 and (c) Al_2O_3 nanoparticles

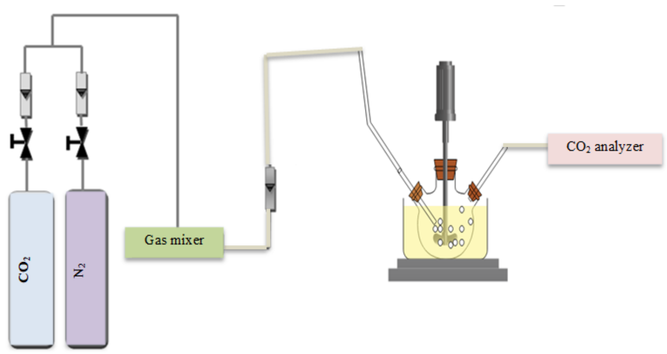


Figure 3. Schematic diagram of the absorption cell

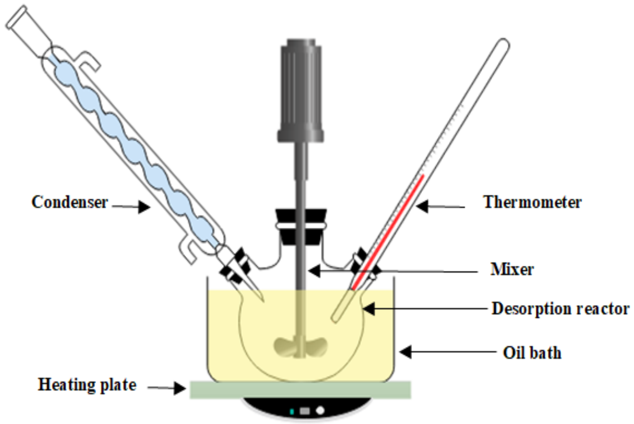


Figure 4. Schematic of the desorption system

The gas outlet from the condenser analyzed using CO_2 analyzer every one minute to identify the maximum nano fluid de-saturation. Moreover, the CO_2 absorption/desorption improvement factor is defined as Eq. (1):

$$I = \frac{CO_2 \text{ absorption/desorption of nano fluid}}{CO_2 \text{ absorption/desorption BBAAS}} \qquad (1)$$

3.3 Analysis procedure

The quantity of the absorbed/desorbed CO_2 was estimated by determining the weight difference between the cells before and after each run. The no more CO_2 absorbed/desorbed was indicating by using the CO_2 analyzer. Also, the CO_2 absorption/desorption rate of the Nano fluid were determined by recording the weight at regular time [10]. Figure 5 showed the analysis procedure.

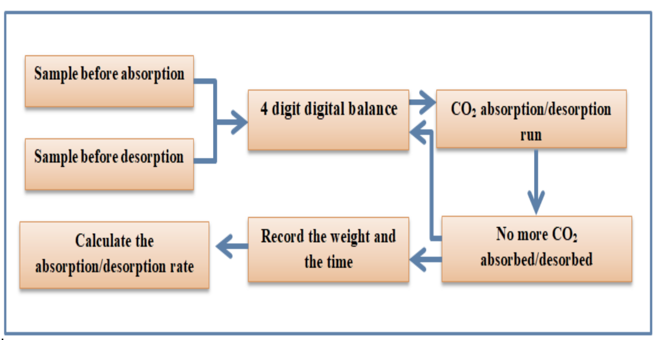


Figure 5. The flow chart of CO_2 analysis procedure

4. RESULTS AND DISCUSSION

4.1 Effect of nano particles on the absorption rate

The adding of different nanoparticles to the 3M MEA/3M TEA on the absorption rate is presented in Figure 6. It can be seen that all the examined nano fluid affects the CO_2 absorption rate progressively. It was found that the CO_2 absorption rate was at lowest value when the 3M MEA/3M TEA was used without any nanoparticles (0.0013 g CO_2 /s). Figure 5 also shows that the nanoparticles concentration range (0.005 – 0.15) vol. % improved the absorption rate remarkably: the addition of Al_2O_3 nanoparticles was higher than the influence of adding both Fe_2O_3 and SiO_2. Besides, the nanoparticles concentration range (0.005-0.01) vol. % led to increasing the rate of CO_2 absorption and descent when the concentration goes above 0.1.

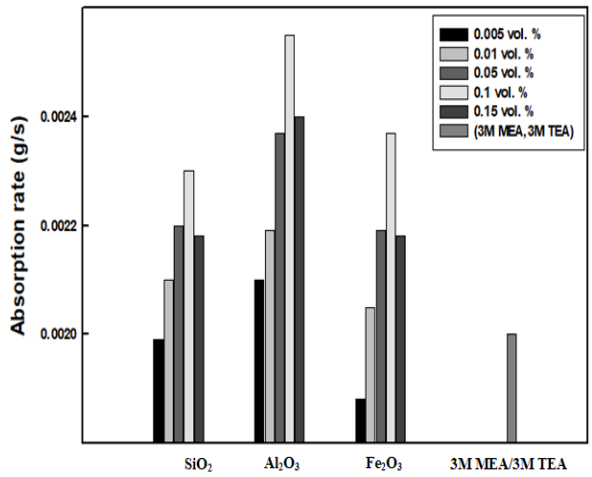


Figure 6. Absorption comparison of the Nano fluid of SiO_2, Al_2O_3 and Fe_2O_3 nanoparticles with different concentration, vol. %

As shown in Figure 7 the results revealed that the concentration of nanoparticles has a significant effect on the absorption rate.

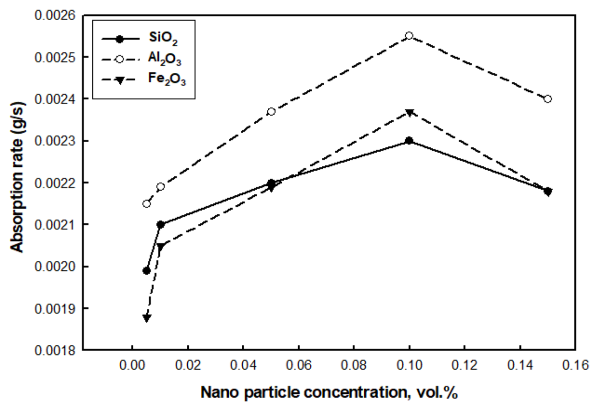


Figure 7. Absorption rate of the nano fluid of SiO_2, Al_2O_3 and Fe_2O_3 nanoparticles with different concentration, vol.%

In addition, the absorption improvement factor was also calculated and shown in Figure 8. It is clear that the addition of nanoparticle enhances the absorption rate significantly. The SiO_2 nanoparticles have the best improvement with over than 1.3 compared to that of Al_2O_3 and Fe_2O_3 nanoparticles in all vol%. Moreover, the effect of nanoparticles percentage addition was very important factor that influence the improvement inversely when increase over 0.1%. The addition of more nanoparticles may lead to absorbing more CO_2. However, in this case the adsorption capacity of nanoparticles and the area of the gas-liquid interface will be limited [11]. Besides, the viscosity of nano fluid it's another important property which adversely affected by increase of nanoparticles.

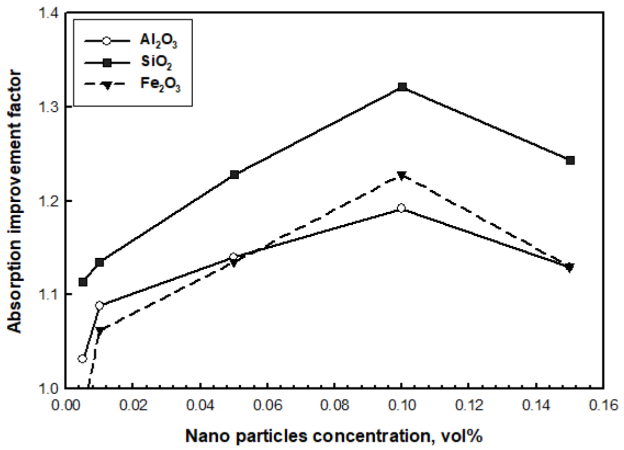
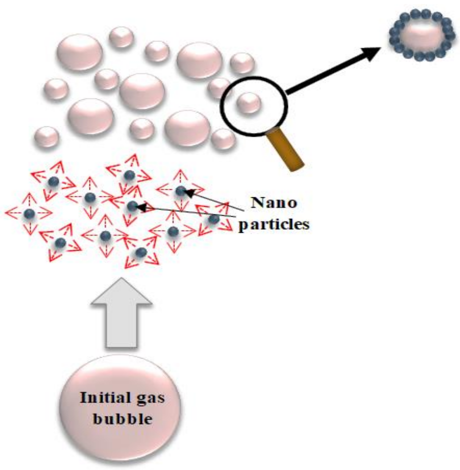
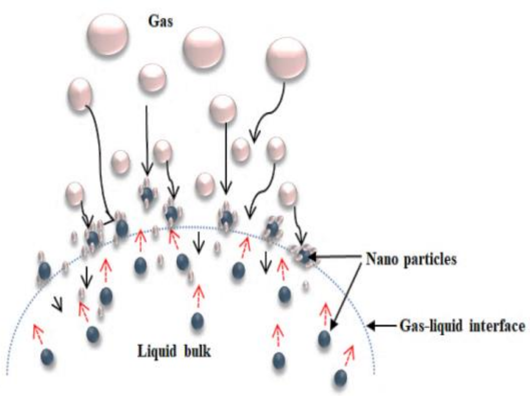


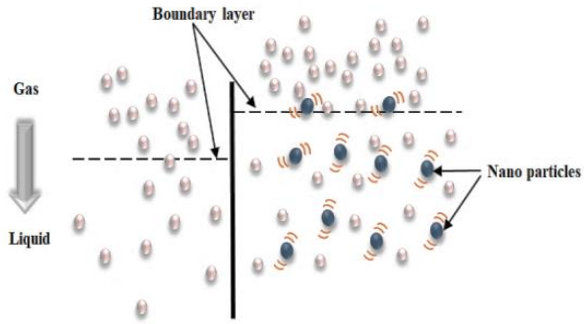
Figure 8. Improvement factor of CO_2 absorption rate in the nano fluid of SiO_2, Al_2O_3 and Fe_2O_3 nanoparticles with different concentration vol.%



(a) The effect of bubble breaking



(b) shuttle effect



(c) boundary mixing effect

Figure 9. Schematic diagram of the absorption mechanism by nanofluid

The absorption behavior of CO_2 by nano fluids has not been described completely yet. The most accepted theories were the effect of bubble breaking the effect of boundary mixing and the shuttle effects that schemed in Figure 9.

The first behavior is the effect of bubble breaking shown in Figure 9(a), in this theory the gas enters the liquid phase as small bubble by using nozzle with a high gas/liquid midst area. When the bubble flows in the liquid, the crashes occur. The merging of the bubbles in the gas liquid diffusions is reserved by the presence of nanoparticles. These particles crash with the gas bubbles that inhibit the combination of the bubbles. This behavior is founded depending on the fact that the specific interfacial area can be increased due to the addition of nanoparticles that affecting the overall mass transfer coefficient. The small bubbles size in the nanofluids were visualized and compared with the absorbent without nanoparticles [12].

The second theory, denotes as the shuttle effect as shown in Figure 9(b). This theory supposes that the nanoparticles in the liquids act as vehicles to transport more CO_2 from the interface of the gas/liquid to the bulk of the liquid. The nanoparticles with high ability of the adsorption adsorb CO_2 in the gas phase through the flow of the diffusion and desorb in the bulk of the liquid. Then, the nanoparticles return to the area of high CO_2 concentration to re transfer and this repeated over and over. This behavior is important even in case of low nanoparticles concentration as a result of the high surface area that offered by nanoparticles [12]. The last theory is the effect of hydrodynamic or the effect of boundary mixing behavior as shown in Figure 9(c). This mechanism is depending on the nanoparticles effect which decrease the boundary layer of the mass transfer by re mix to get active liquid film. This suggestion is about the sturdy micro-convection movement and Brownian motion of the nanoparticles [7, 13].

4.2 Effect of nano-particles on the desorption rate

Figure 10 displays the effect of the presence of nanoparticles (Al_2O_3, SiO_2 and Fe_2O_3) on the desorption rate of CO_2. The result revealed that the CO_2 desorption rate increases with increasing the amount of nanoparticle. As displayed the effect of adding more Al_2O_3, SiO_2 nanoparticles on the desorption rate was less than the effect of adding more Fe_2O_3 nanoparticles.

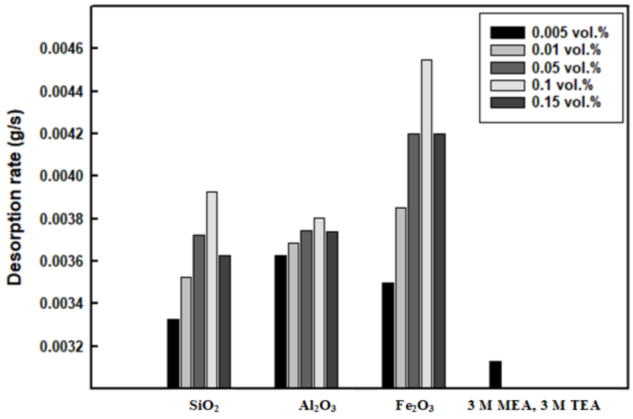


Figure 10. Desorption comparison of the Nano fluid of SiO_2, Al_2O_3 and Fe_2O_3 nanoparticles with different concentration, vol. %

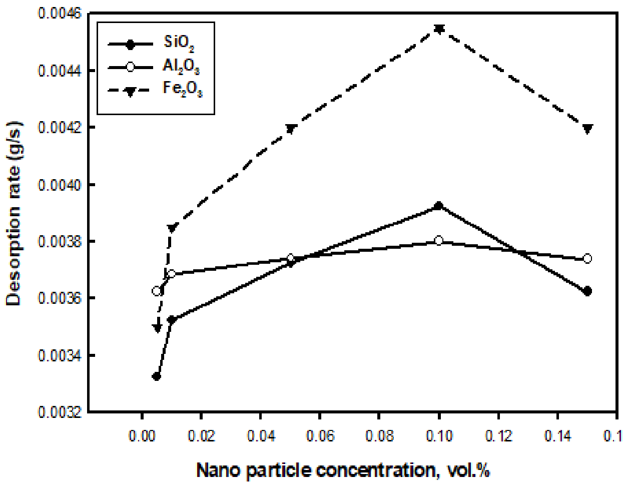


Figure 11. Desorption rate of the CO_2 absorption rate in the nano fluid of SiO_2, Al_2O_3 and Fe_2O_3 nanoparticles with different concentration, vol. %

Figure 11 shows the effect of nano fluids on the CO_2 desorption rate at different fluid concentration. It can be seen that the desorption rate was lowest when the solvent used without nanoparticles (0.003 gCO_2/s). Besides, the desorption rate effected proportionally with the nanoparticles at (0.005-0.15) vol. % and adversely when the nanoparticles exceed 0.15 vol. %. Moreover, the result shows that the desorption rate was higher than that of absorption caused by decreasing the stability of the nano fluid after absorption process. These changes in properties depends on the physical interaction between the nanoparticles and the solvent such: decreasing the thickness of the diffusion boundary layer by changing the fluid properties. For example, the effect of increasing viscosity shown by Yang [14], increasing of the Brownian motion due to increase the radius of nanoparticle movement; effecting the interaction of the nanoparticles which affect their motion [13], increase the contact between the gas and liquid lead to increase the self-diffusion [15, 16].

The CO_2 desorption improvement factor was determined and plotted against the nanoparticles concentration for each nano fluid as shown in Figure 12. It's clear that adding nanoparticles to the solvent significantly improve the CO_2 desorption rate due to the theories described below.

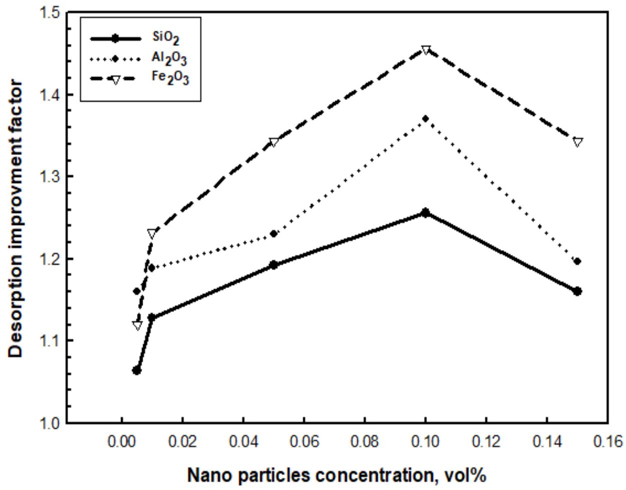


Figure 12. Improvement factor of CO_2 desorption rate in the nano fluid of SiO_2, Al_2O_3 and Fe_2O_3 nanoparticles with different concentration, vol. %

The improvement of CO_2 desorption rate can be described by some possible mechanisms as follow [17-21].

The impact of surface on nanoparticles, CO_2 desorption process can be considered as a boiling process to clarify the mechanism [21]. Generally, the state of boiling process involves creating bubbles due to increasing temperature of the fluid, which leads to phase change. The presence of nanoparticles affects the properties of heat transfer boiling surface [17, 21]. The nanoparticles in the solvent settle down on the surface of the heater due to gravity and the common convection, the nanoparticles. Generally, an increase in the temperature above the saturation point leads to boiling process. However, according to Henry's solubility law the slight increase in the temperature causes renewal bubble [21].

- The mechanism of activation energy, which is affected by nanoparticles motion. On the level of nano measure the liquid molecules collides with the nanoparticles. An increase in the temperature leads to increasing the activation energy of the nanoparticles. As a result, the liquid molecules are more effective due to the energy gained. Therefore, the collision between liquid molecules and nanoparticles increases the activation energy of desorption. Consequently, the nanoparticles and molecules of CO_2 gas crash then the CO_2desorption rate improves [17].
- The effect of nanoparticles on the thermal conductivity [17]. The improvement of the nano fluid's heat transfer mechanism studied widely. Also, many explanations of heat transfer mechanism were reported such as the nature of heat transport, the Brownian motion, layering of the molecular-level and the impact of nanoparticles grouping excreta [16, 17].

So far, these performances have not been proven up. However, many experiments and statistics research that studied the effect of nanoparticles on the thermal conductivity have made this behavior as a fact [17]. The heat transfer is affected by the distribution of nanoparticles in the solvent. Increasing the temperature leads to making the desorption process faster than the base fluid which causing improvement in the CO_2 desorption rate [19].

5. CONCLUSIONS

This study examined the influence of nanoparticles on the mass and heat transfer through a process of CO_2 absorption/ desorption using a blend of MEA and TEA as a base solvent. The results showed that most of the used nanoparticles improved the rate of CO_2 absorption/desorption significantly. Under the same conditions, the improvement factor of CO_2 absorption/desorption in the nano fluids increased with increasing the nanoparticles concentrations to a highest value, 0.1%, then decreased. Also, it was found that the order of the nano fluids solutions which improved the absorption rate were: $SiO_2 > Fe_2O_3 > Al_2O_3$ solution. On the other hand, the order of the improvement of CO_2 desorption rate factors were: $Fe_2O_3 > Al_2O_3 > SiO_2$.

Furthermore, all possible mechanisms were described concisely to verify that the 3M MEA/3M TEA /nano fluid were prepared to promise a new technique that can improve both mass and heat transfer.

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REFERENCES

[1] Wiheeb, A.D., Shakir, S.W., Ahmed, M.A., Rajab, E.A. (2018). Experimental investigation of carbon dioxide capturing into aqueous carbonate solution promoted by alkanolamine in a packed absorber. In 2018 1st International Scientific Conference of Engineering Sciences-3rd Scientific Conference of Engineering Science (ISCES), pp. 152-156. https://doi.org/10.1109/ISCES.2018.8340545

[2] Ochedi, F.O., Yu, J., Yu, H., Liu, Y., Hussain, A. (2020). Carbon dioxide capture using liquid absorption methods: A review. Environmental Chemistry Letters, 1-33. https://doi.org/10.1007/s10311-020-01093-8

[3] Gao, H., Wu, Z., Liu, H., Luo, X., Liang, Z. (2017). Experimental studies on the effect of tertiary amine promoters in aqueous monoethanolamine (MEA) solutions on the absorption/stripping performances in post-combustion CO_2 capture. Energy & Fuels, 31(12): 13883-13891. https://doi.org/10.1021/acs.energyfuels.7b02390

[4] Wiheeb, A.D., Shakir, S.W., Othman, M.R. (2018). Synthesis and characterization of mesoporous hydrotalcite-alumina membrane for carbon dioxide enrichment. In IOP Conference Series: Materials Science and Engineering, 454(1): 012107. https://doi.org/10.1088/1757-899X/454/1/012107

[5] Zheng, Y., Yang, H., Fazilati, M.A., Toghraie, D., Rahimi, H., Afrand, M. (2020). Experimental investigation of heat and moisture transfer performance of $CaCl_2/H_2O-SiO_2$ nanofluid in a gas–liquid microporous hollow fiber membrane contactor. International Communications in Heat and Mass Transfer, 113: 104533. https://doi.org/10.1016/j.icheatmasstransfer.2020.104533

[6] Zoghi, A.T., Feyzi, F., Zarrinpashneh, S. (2012). Experimental investigation on the effect of addition of amine activators to aqueous solutions of N-methyldiethanolamine on the rate of carbon dioxide absorption. International Journal of Greenhouse Gas Control, 7: 12-19. https://doi.org/10.1016/j.ijggc.2011.12.001

[7] Keshishian, N., Esfahany, M.N., Etesami, N. (2013). Experimental investigation of mass transfer of active ions in silica nanofluids. International Communications in Heat and Mass Transfer, 46: 148-153. https://doi.org/10.1016/j.icheatmasstransfer.2013.05.014

[8] Ashrafmansouri, S.S., Esfahany, M.N. (2014). Mass transfer in nanofluids: A review. International Journal of Thermal Sciences, 82: 84-99. https://doi.org/10.1016/j.ijthermalsci.2014.03.017

[9] Liu, F., Jing, G., Lv, B., Zhou, Z. (2017). High regeneration efficiency and low viscosity of CO_2 capture in a switchable ionic liquid activated by 2-amino-2-methyl-1-propanol. International Journal of Greenhouse Gas Control, 60: 162-171. https://doi.org/10.1016/j.ijggc.2017.03.017

[10] Kim, H., Rajamanickam, R., Park, J.W. (2017). Carbonation and decarbonation of non-aqueous solutions with different compositions of ethylene glycol and various amidines. International Journal of Greenhouse Gas Control, 59: 91-98. https://doi.org/10.1016/j.ijggc.2017.02.012

[11] Lee, J.W., Pineda, I.T., Lee, J.H., Kang, Y.T. (2016). Combined CO_2 absorption/regeneration performance enhancement by using nanoabsorbents. Applied Energy, 178: 164-176. https://doi.org/10.1016/j.apenergy.2016.06.048

[12] Jeong, M., Lee, J.W., Lee, S.J., Kang, Y.T. (2017). Mass transfer performance enhancement by nanoemulsion absorbents during CO_2 absorption process. International Journal of Heat and Mass Transfer, 108: 680-690. https://doi.org/10.1016/j.ijheatmasstransfer.2016.12.073

[13] Jiang, J., Zhao, B., Cao, M., Wang, S., Zhuo, Y. (2013). Chemical absorption kinetics in MEA solution with nano-particles. Energy Procedia, 37: 518-524. https://doi.org/10.1016/j.egypro.2013.05.138

[14] Yang, L., Du, K., Niu, X.F., Cheng, B., Jiang, Y.F. (2011). Experimental study on enhancement of ammonia–water falling film absorption by adding nano-particles. International Journal of Refrigeration, 34(3): 640-647. https://doi.org/10.1016/j.ijrefrig.2010.12.017

[15] Turanov, A.N., Tolmachev, Y.V. (2009). Heat-and mass-transport in aqueous silica nanofluids. Heat and Mass Transfer, 45(12): 1583-1588. https://doi.org/10.1007/s00231-009-0533-6

[16] Meisam, A., Ahmad, A., Hamed, M. (2019). Experimental investigation of metal oxide nanofluids in a plate heat exchanger. Journal of Thermophysics and Heat Transfer, 33(4): 994-1005. https://doi.org/10.2514/1.T5581

[17] Fan, J., Wang, L. (2011). Review of heat conduction in nanofluids. Journal of Heat Transfer, 133(4): 040801. https://doi.org/10.1115/1.4002633

[18] Veilleux, J., Coulombe, S. (2011). A dispersion model of enhanced mass diffusion in nanofluids. Chemical Engineering Science, 66(11): 2377-2384. https://doi.org/10.1016/j.ces.2011.02.053

[19] Pang, C., Jung, J.Y., Lee, J.W., Kang, Y.T. (2012). Thermal conductivity measurement of methanol-based nanofluids with Al_2O_3 and SiO_2 nanoparticles. International Journal of Heat and Mass Transfer, 55(21-22): 5597-5602. https://doi.org/10.1016/j.ijheatmasstransfer.2012.05.048

[20] Yoon, S., Chung, J.T., Kang, Y.T. (2014). The particle hydrodynamic effect on the mass transfer in a buoyant CO_2-bubble through the experimental and computational studies. International Journal of Heat and Mass Transfer, 73: 399-409. https://doi.org/10.1016/j.ijheatmasstransfer.2014.02.025

[21] Ham, J., Kim, H., Shin, Y., Cho, H. (2017). Experimental investigation of pool boiling characteristics in Al_2O_3 nanofluid according to surface roughness and concentration. International Journal of Thermal Sciences, 114: 86-97. https://doi.org/10.1016/j.ijthermalsci.2016.12.009

NOMENCLATURE

Symbol	description	Unit
M	molarity	Mol/l

Abbreviations

Al_2O_3	Aluminum oxide
CO_2	Carbon dioxide
Fe_2O_3	Iron oxide
GHGs	Greenhouse gases
MEA	Monoethanolamine
DEA	Diethanolamine
SiO_2	Silicon oxide
TEA	Triethanolamine
PZ	Piperazine
AMP	2-amino-2-methyl 1-propanol