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ORIGINAL RESEARCH PAPER

# Study on Mass Transfer Enhancement in a Gas-Liquid System Using Nanomaterials

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**Abstract**

The main objective of this paper is to examine the effect of nanomaterials on mass transfer coefficient in bubble type absorption of carbon dioxide by experiment. The absorption process is carried out in a bubble column and in room temperature. Mass transfer coefficient, saturated concentration of $CO_2$, and gas holdup are determined in this system. The kinds of nanomaterials, the concentrations of each one and the gas superficial velocity are considered as the key parameters. The results show that the mass fraction of nanomaterials has an optimum value to the mass transfer coefficient and saturated concentration of $CO_2$. 0.07% CNT nanofluid increases the mass transfer coefficient up to 78%. The superficial velocity of $CO_2$ enhances mass transfer coefficient and gas holdup within the experimental range, whilst it has no effect on saturated concentration of $CO_2$. In addition, nanomaterials in solution increase the gas holdup.

## 1. Introduction

In absorption processes, several techniques have been the key subject to enhance heat and mass transfer processes and obtain better performance of multiphase system within the recent years[1].

The techniques for the improvements are generally classified into mechanical treatment (such as heat transfer mode, the phases contact mode), the chemical treatment (such as additive adding) and the fluid properties improvement [2]. According to Kang et al. [3] experiment, the size of bubble absorber could be47% smaller than that of falling film absorber in the absorption performance of $NH_3/H_2O$.Adding of surface active agents into the liquid phase is a case of chemical treatment.

Surfactant changes the interfacial turbulence of the fluid that improves the heat and mass transfer coefficients.

Recently, nanofluids are known as one of the effective heat and mass transfer media[2]. Since the term ‘‘nanofluid’’ for enhancing heat transfer was firstly used by Choi [4], a large number of experimental studies have been performed on the investigating nanofluids with practical application to heat transfer[5].

A nanofluid is a suspension in which nanoparticles ($d_p$<100 nm) are suspended uniformly in a base fluid[4].

Krishnamurthy et al. [6] first observed that a dye diffuses faster in a nanofluid than in water.

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**Nomenclature**

| | | | |
|---|---|---|---|
| | | $Q_g$ | Gas flow rate (L/min) |
| $C_A$ | Gas concentration in the liquid phase (g/L) | $R_{eff}$ | Effective ratio of nanofluid (-) |
| $C_{As}$ | Saturated gas concentration in the liquid phase (g/L) | u | Gas superficial velocity (m/s) |
| H | Height of nanofluid in the absorber (Cm) | t | Dwell time (min) |
| $H_0$ | Initial height of nanofluid in the absorber (Cm) | $\varepsilon_g$ | Gas hold up(-) |
| $k_{La}$ | Volumetric mass transfer coefficient (1/min) | | |

They explained that the Brownian motion of the nanoparticles induces convection in the nanofluids.

One of the most important applications of nanofluids in gas absorption is $CO_2$ removal from flue gases. $CO_2$ is one of the greenhouse gases which its control is becoming more important nowadays. Numerous studies have been carried out to enhance the $CO_2$ removal efficiency.

Astarita [7] used a Mono Ethanol Amine (MEA) solution to enhance the absorption performance by a reaction between the MEA and $CO_2$. Rao [8] perform the Hot Potassium Carbonate (HPC) process. Cullinane and Derks [9, 10] used a piperazine material to enhance the $CO_2$ absorption. Dagaonkar et al.[11] were the first researcher that reported the rate of gas absorption in a liquid phase may be enhanced considerably by the presence of particles in the liquid-phase. They added $TiO_2$microparticles to water to absorb $CO_2$.

In recent decade, nanofluid is known for its high thermal conductivity properties, and is can be used to enhance the heat and mass transfer processes of absorption.

In this research the effects of nanoparticles are investigated on the mass transfer enhancement in absorption of $CO_2$ in a bubble column system. Three types of nanostructural materials including CNT, $TiO_2$, and $SiO_2$ are used and the influences of mass fraction of nanomaterials and gas superficial velocity on mass transfer coefficient are studied.

## 2. Material and Method

### 2.1. Experimental study

Figure 1 shows the schematic diagram of the bubble absorption equipment.

The experimental setup consists of a cylindrical absorber test section with the diameter of 50 mm and length of 410 mm. Since the bubble-type absorber operates in the batch mode, the absorption process operates in unsteady-state until it saturates. Volume of the nanofluid (as absorber) was fixed to 0.6 L at the room conditions during the experiments. The purity of $CO_2$ gas is 99.99 %.

The nanoparticles with a specific dosage are mixed and fully dispersed with the distilled water before the solution is charged into the nanofluid tank.

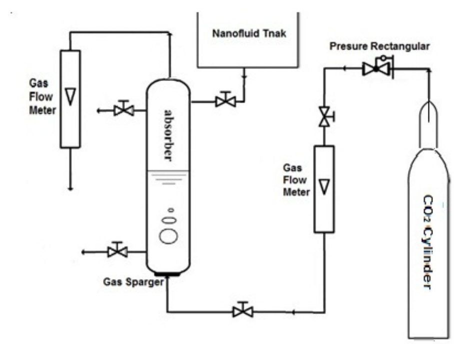


**Fig. 1.** Schematic diagram of the bubble absorption equipment

For the stable distribution of nanomaterials, the nanofluids are stirred for 20 hours and then be treated by the ultrasonic bath (Parsonic 2600) for 2 h. The nanofluid is filled up to a fixed volume in the nanofluid tank and then is discharged to the bubble absorber. Thereafter absorption begins when $CO_2$ enters the bubble absorber through a ceramic perforated plate sparger, which is located at the bottom of the absorber. The flow rate of $CO_2$ is measured by the gas flowmeter.

The gas flow rate is adjusted to allow the superficial gas velocity to be low enough in order to remaining in bubbly regime. The absorption rate is calculated by measuring the $CO_2$ concentration of the nanofluids using titration method. In this method, at first 5 mL of sample is mixed with 10-20 mL of sodium hydroxide, then a few drops of phenolphthalein are added to the solution as indicator, and hydrochloric acid is used as titrator to remove the pink color of the solution. In the next step, a few drops of methyl orange are added to the solution and titration is continued until the orange color of the solution is changed to yellow.

This point is the equivalent and the used amount of hydrochloric acid indicates the concentration of $CO_2$ in the solution. In case of CNT nanofluids, due to the black color of the solution the equivalent point is determined by the changes in pH of the solution. All experimental data are repeatable with a negligible error.

In the experiments three kind of nanostructure material are used to prepare nanofluids. The properties of the nanomaterials are summarized in table 1.

In this study, different mass fractions of nanomaterials are experimented. The nanofluid containing $TiO_2$ and $SiO_2$ nanoparticles are prepared with 0.01, 0.05, 0.1 and 0.5 Wt. %, while CNTs are added with 0.01, 0.05, 0.07 and 0.1 Wt. %.

**Table 1**
Properties of nanomaterials.

| Nano material | Producer | Average Size (nm) | Surface area ($m^2$/g) |
|---|---|---|---|
| CNT | RIPI | D=10-30, L=100 | 105 |
| TiO2 | Degussa | 21 | 50 |
| SiO2 | Degussa | 12 | 200 |

## 2.2. Modeling study

The mass balance on liquid phase of the bubble column leads to the ordinary differential equation1 assuming perfect mixing, mass transfer between two phases without reaction in the unsteady state.

$$\frac{dc_A}{dt} = k_L a(c_{As} - c_A) \quad (1)$$

Where $C_A$ is $CO_2$ concentration in the liquid phase, $C_{AS}$ is the saturated concentration of $CO_2$ in the liquid phase and $k_La$ is the volumetric mass transfer coefficient. Solving the equation 1 results equation2to obtain the mass transfer coefficient

$$c_A = c_{As}(1 - \frac{1}{e^{k_L a\, t}}) \quad (2)$$

The volumetric mass transfer coefficient ($k_La$) is determined by plotting the experimental $C_A$ values versus time, while $C_{As}$ has a fixed amount for any nanofluid. Differentiation of equation 2 results to the rate of absorption as a function of time as equation 3.

$$\frac{dC_A}{dt} = k_L a C_{As} e^{-k_L at} \quad (3)$$

In order to analyze the effect of nanofluid on the mass transfer rate, the effective ratio ($R_{eff}$) is defined as equation 4.

$$R_{eff} = \frac{(k_L a)_{nanofluid}}{(k_L a)_{water}} \quad (4)$$

The physical meaning of the effective ratio is ‘the effectiveness of the nanofluid for mass transfer coefficient enhancement. Amount of this parameter shows how much the nanoparticles improve the mass transfer coefficient.

For the bubble column experiments, the gas holdup that varies with gas velocity and nanoparticle concentrations is measured using the liquid expansion method, which is indicated in the equation 5.

In this method, the initial liquid height in the column and the height after gassing the column are measured. The gas hold up is calculated by using following equation:

$$\varepsilon_g = \frac{H - H_0}{H} \quad (5)$$

In this equation$H_0$ is the initial height of nanofluid and H is the height of nanofluid after entering $CO_2$ into the column.

# 3. Results and Discussion

## 3.1. Effect of mass fraction of nanomaterials on absorption amount

Figures (2-4) display the experimental data of $CO_2$concentration in the liquid phase during the time in different dosage of CNT.

As it is observed the absorption amount increases with increasing of the nanoparticles mass fraction sharply at first, then gradually fix. From figure 2 it can be understood that the 0.07% CNT nanofluid has the maximum absorption amount.

Figures 3 and 4 demonstrate that in $TiO_2$ nano-fluids, the maximum amount of $CO_2$ is absorbed when 0.05% of $TiO_2$ and 0.1% 0f $SiO_2$ nanoparticles are added to distilled water.

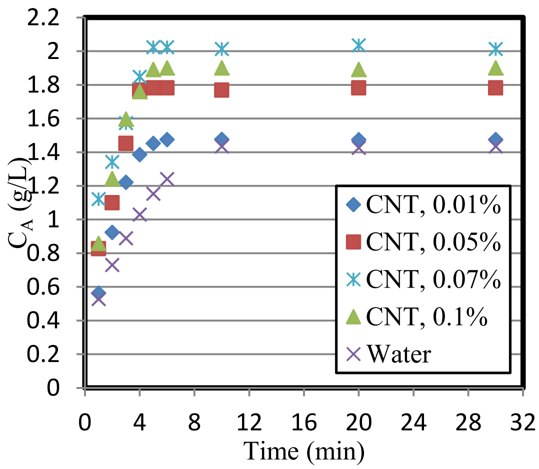


**Fig. 2.** Variation of $CO_2$ concentration in liquid phase with time in different CNT dosage ($Q_g$=0.5 L/min)

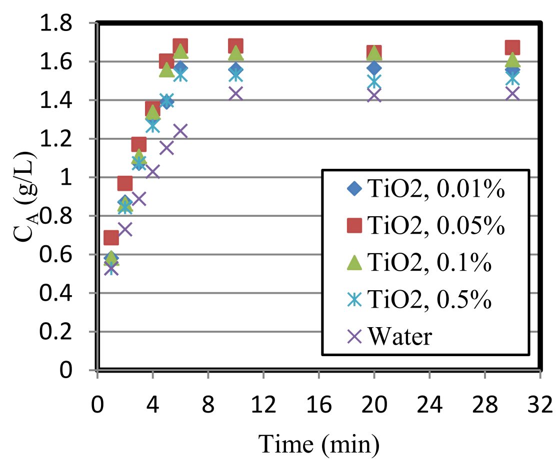


**Fig. 3.** Variation of $CO_2$ concentration in liquid phase with time in different $TiO_2$ nanoparticle dosage ($Q_g$=0.5 L/min)

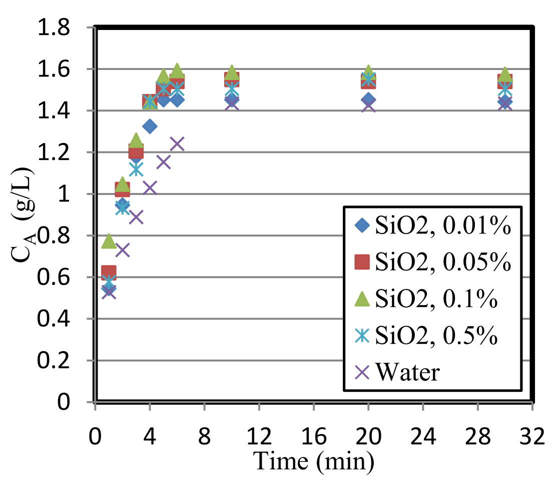


**Fig. 4.** Variation of $CO_2$ concentration in liquid phase with time in different $SiO_2$ nanoparticle dosage ($Q_g$=0.5 L/min)

The nanoparticles can be agglomerate at high dosage and in this condition increasing in the nanoparticle dosage do not improve the $CO_2$ removal. This can be reason of selection of no higher dosage as the optimum dosage in the $Co_2$ removal.
In addition, the absorption amount of carbon dioxide in liquid phase increases to an approximate constant amount, which is the saturation concentration of $CO_2$. The use of nanomaterials increases the saturation of $CO_2$. The values of $CO_2$ saturated concentration in nanofluids with optimum mass fraction of nanomaterials are illustrated in table 2.

It can be concluded that 0.07% CNT nanofluid absorbs the maximum amount of $CO_2$. This nanofluid enhances the saturated concentration of $CO_2$ up to 40%.

## 3.2. Effect of mass fraction of nanomaterials on volumetric mass transfer coefficient

The volumetric mass transfer coefficient ($k_La$) is calculated for water and each nanofluid using curve fitting of experimental data presented in figures (2-4) in equation 2. All $R^2$ values of curve fittings are more than 98%, therefore the selected model is seemed to be accurate.

These correlations give term ($k_La$) for $CO_2$ removal using nanofluids. Then the effective ratio is determined from equation4. Figure 5 expresses the effective ratio with respect to the mass fraction of CNT, $TiO_2$ and $SiO_2$ nanoparticles.

**Table 2**
Gas phase reactions [21].

| **nanomaterial** | **CNT** | **$SiO_2$** | **$TiO_2$** |
|---|---|---|---|
| Optimum Mass fraction (%) | 0.07 | 0.05 | 0.1 |
| CAs (g/L) | 2.046 | 1.697 | 1.597 |

Since the effective ratios of all nanofluids are higher than1.0, it is undoubtedly implied that nanofluids can enhance the mass transfer coefficient, so improve the absorption performance.

It also can be inferred that the effective ratio increases with the mass fraction of nanofluids increasing at first, then decreases. The maximum effective ratio is 1.78 in the case of nanofluid with 0.07% carbon nanotubes.

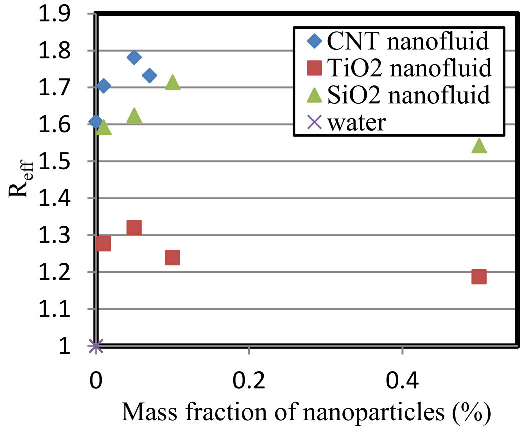


**Fig. 5.** Effective ratio in different nanoparticles dosage in the liquid phase ($Q_g$=0.5 L/min)

3.3. Effect of mass fraction of nanomaterials on absorption rate

The rate of absorption ($dC_A/dt$) is determined based onequation3usingcalculated data $K_la$, and $C_{As}$.

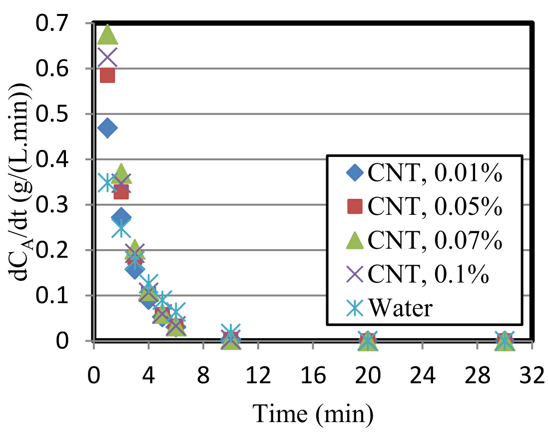


**Fig. 6.** Absorption rate in different concentrations of CNT nanofluid ($Q_g$=0.5 L/min)

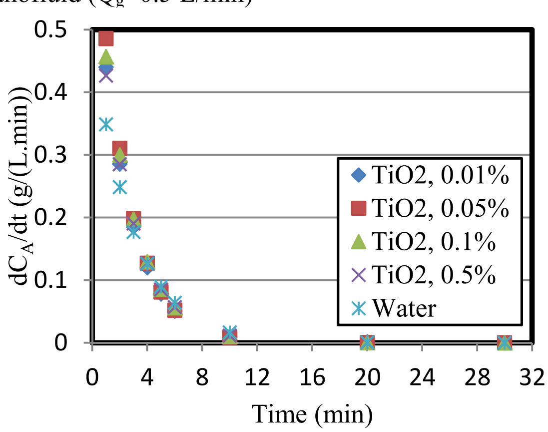


**Fig. 7.** Absorption rate in different concentrations of $TiO_2$nanofluid ($Q_g$=0.5 L/min)

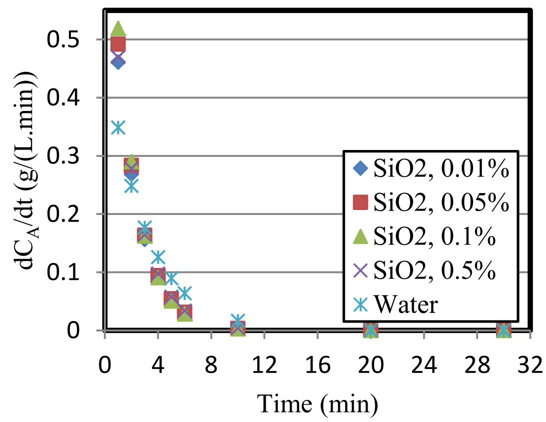


**Fig. 8.** Absorption rate in different concentrations of $SiO_2$ nanofluid ($Q_g$=0.5 L/min)

Figures 6 to 8 show the absorption rate versus time in water and nanofluids.

As it is observed in these figures the absorption rate was decreased by the time due to the absorber of a batch system. The absorption rate increases with the mass fraction of nanomaterials increasing at first, then it gradually fix. The mechanisms of the nanofluid enhancing bubble absorption have four possible factors as follows.

Nanomaterials in the nanofluids can cause the micro-convection in liquid phase because of the Brownian motion of nanomaterials. This micro-convection can improve the mass diffusion of $CO_2$ gas in the nanofluid. According to the Krishnamurthy's experiment [6], the enhancement of the diffusion coefficient firstly increases with the mass fraction of the nanoparticles increasing, and then decreases. Nanomaterials in the nanofluid can cause the grazing effect, which was described by Kars et al. [12] and Alper et al. [13].

The grazing effect is that the particles in the liquid adsorb gas molecules in the gas–liquid interface, then move right through the concentration boundary layer, finally pick up the adsorbate in the bulk liquid. According to Reference [12], the enhancement of the grazing effect on absorption firstly increases with increasing the mass fraction of particles, and then remains constant.

The effects of the concentration of nanomaterials on the enhancement of mass diffusion and grazing effect can explain just the deviating trend of the absorption rate with the mass fraction of nanomaterials. Fan et al. [14] found that the gas holdup in the nanofluid is higher than that of water at the same flow rate of the gas.

The increase in the gas holdup can lead to an increase in the area of the gas–liquid interface for the same flow rate of $CO_2$ gas. Therefore improve the absorption rate of the $CO_2$. Nanoparticles in the nanofluid can increase the thermal conductivity of liquid phase and the heat transfer in the absorption process. Absorption process is a combined heat and mass transfer process.The improvement of heat transfer can decrease the temperature at the gas–liquid interface; increase the absorption potential of liquid phase. So enhance the absorption rate of the $CO_2$.

## 3.4. Effect of type of nanomaterials on gas holdup

The gas holdup is a main factor in characterization of the bubble column operation. Table 3 demonstrates the gas holdup values obtained by using equation 5, in different nanofluids.

**Table 3**
Gas holdup in mass fraction 0.1% nanomaterial.

| Liquid Phase | Distilled water | CNT | $TiO_2$ | $SiO_2$ |
|---|---|---|---|---|
| εg | 00.015 | 0.017 | 0.018 | 0.020 |

The results indicate that the gas holdup in the nanofluid is consistently higher than that in water. According to Fan et al.[14] the difference in the gas holdup between the nanofluid and water in the bubble column experiment can be related to the differences in bubble size. They found that the bubble size in nanofluids is smaller than in water, and the smaller bubbles results in larger gas holdup. In our experiment 0.1% of $SiO_2$ nanoparticles in water caused the maximum gas holdup.

## 3.5. Effect of superficial gas velocity on absorption amount

Figures (9-11) reveal the absorption amount of $CO_2$ in nanofluid for the different superficial gas velocities. The flow rates of $CO_2$ are adjusted to 0.5, 1 and 1.5 L/min, which results to superficial gas velocities of 0.004, 0.008 and 0.012 m/s, respectively, and the mass fraction of nanomaterials in the nanofluids is 0.05%.
The experimental data show that slope of the curve which is the absorption rate is increased with increasing superficial gas velocities for each nanomaterial.

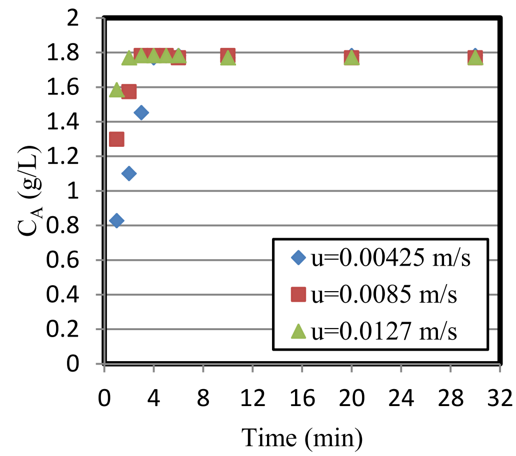


**Fig. 9.** $CO_2$ concentration in 0.05% CNT nanofluid in different superficial gas velocities

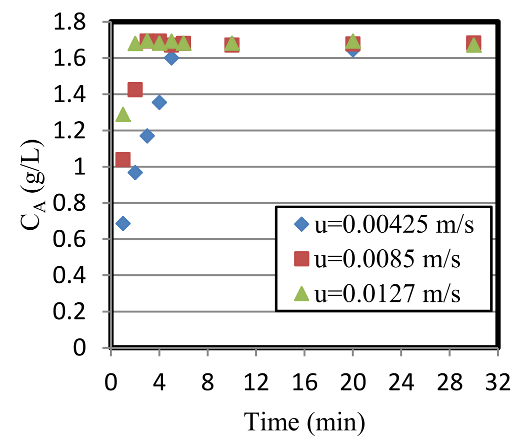


**Fig. 10.** $CO_2$ concentration in 0.05% $TiO_2$nanofluid in different superficial gas velocities

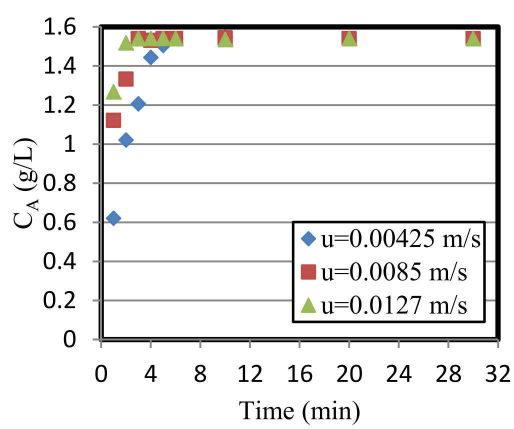


**Fig. 11.** $CO_2$ concentration in 0.05% $SiO_2$nanofluid in different superficial gas velocities

This indicates that mass transfer rate and time of saturation are affected by the superficial gas velocity of the gas, although the saturated concentration of $CO_2$ does not change with the velocity.

### 3.6. Effect of superficial gas velocity on volumetric mass transfer coefficient

The superficial gas velocity as another main factor affecting in the column operation is calculated as dividing the inlet gas volumetric flow rate to the column section area. Figure 12 shows the mass transfer coefficient in water and optimum concentration of nanofluids in different superficial velocities of $CO_2$.
The mass transfer coefficient increases almost linearly with increasing the superficial gas velocity. The superficial gas velocity affects the grazing effect because of variation of the disturbance of the nanofluid [1]. Thus the increase of superficial velocity of $CO_2$ improves remarkably the grazing effect of the nanofluids.

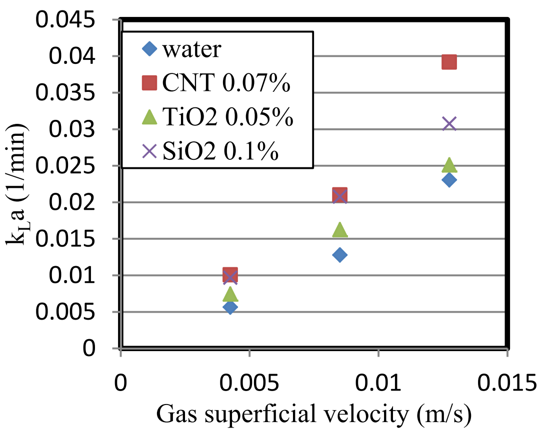


**Fig. 12.** Mass transfer coefficient in different superficial gas velocities

### 3.7. Effect of superficial gas velocity on gas holdup

The present experimental study reveals the superior gas hold up in nanofluids. It is also observed that the gas holdup in a bubble column increases significantly when superficial gas velocity increases. This behavior is remarkable for nanomaterials related to water and $SiO_2$ in comparison with the other nanomaterials. These results are demonstrated in figure 13.

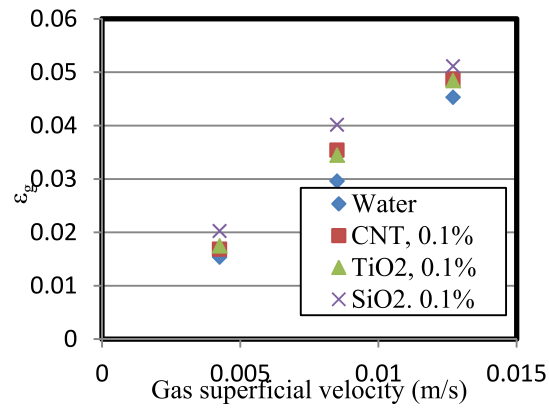


**Fig. 13.** Gas holdup in different superficial velocities in nanofluids and water

## 4. Conclusion

In this study, the $CO_2$ gas absorption using different nanofluids in a bubble column was investigated experimentally. The kinds of nanoparticles and the concentrations of each nanoparticle and the superficial velocity of $CO_2$are considered as the key parameters.

It can be concluded that addition of nanomaterials enhances the mass transfer coefficient and saturation concentration of $CO_2$ in liquid phase and therefore the absorption performance during the bubble absorption process. The maximum effective ratio is 1.78 when 0.07% of carbon nanotubes are added to water. CNT is the most effective nanomaterials among the considered nanomaterials. The mass fraction of nanomaterials has an optimum value to the effective ratio of the nanofluids.

The results also showed that the superficial velocity of $CO_2$enhances mass transfer coefficient within the experimental range.
Gas holdup in nanofluids is higher than water, and increases with increasing nanomaterials concentration and gas superficial velocity. The enhancement mechanism by nanoparticles for absorption performance can be explained by the grazing effect, but the distinct mechanism is not developed yet. The additional analytical study should be carried out to clarify the enhancement mechanism of mass transfer performance.

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