

EXPERIMENTAL STUDIES OF CO₂ ABSORPTION ENHANCEMENT IN WATER-BASED NANOFLUIDS OF CARBON NANOTUBES

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(Submitted: November 1, 2014; Revised: November 2, 2015; Accepted: January 25, 2016)

Abstract – The improvement of CO₂ absorption by CNT nanofluids with deionized water as the base fluid was studied experimentally. The reactor used was a stirred thermostatic reactor, operated batchwise. Pure CO₂ was employed in all the experiments. The content of CNTs in the nanofluids ranged from 0 to 0.2% (wt). The acidification treatment of CNTs was employed to improve the stability of the nanofluids. The parameters, such as the concentration of CNT nanoparticles in the nanofluids, the stirring speed, the ultrasonic time for CNT nanofluid preparation, the nitration time and the amount of nitric acid for CNT acidification were varied. The results show that, with the increase of CNT concentration, the enhancement factor first increased and then leveled off after a certain value of the CNT concentration. With increasing stirring speed, the enhancement factor in stable functional CNT nanofluids declines monotonously, while in poorly dispersed raw CNT suspensions, it first increased and then reduced. The ultrasonic and nitration times and the amount of nitric acid have optimum values for the CO₂ absorption enhancement. The mechanism of the CNT nanofluid enhancement of CO₂ absorption is discussed accordingly. The absorption enhancement by the CNT nanofluid should be mainly attributable to convective motion induced by the Brownian motion and the shuttle effect.

Keywords: Absorption enhancement; nanofluids; CNT; carbon dioxide; mass transfer.

INTRODUCTION

As the main contributor to the greenhouse effect, the control of CO₂ emission into atmosphere has received considerable attention. The technologies to remove CO₂ include absorption, adsorption and gas-separation membranes, etc. (Ghosh et al., 2009; Lin et al., 2009; Lee et al., 2011). However, the membrane method is still in the lab research stage, and too much energy is needed for the adsorption method in the process of desorption (Lee et al., 2011). The chemical absorption technique, in which ethanolamines (Derks et al., 2006; Kucha et al., 2003) are the absorbents commonly used, has the advantage of high absorption rate. Nonetheless, the performance of chemical

absorption is limited by several factors, including the need of much energy for the regeneration of the chemical solvents, oxidative degradation and corrosion issues.

Recent studies found that the gas absorption rate can be increased by using nanofluids (Bahmanyar et al., 2011; Feng and Johnson, 2012; Tang and Zhan, 2011; Manikandan et al., 2012; Yang et al., 2011; Ashrafmansouri and Esfahany, 2014). A nanofluid is defined as a fluid in which nanoparticles below 100 nm in diameter are stably suspended in the base fluid (Keshishian et al., 2013). Krishnamurthy et al. (2006) studied mass diffusion of fluorescein dye in nanofluids by taking time-dependent images. The diffusion coefficient of the dye in Al₂O₃ nanofluids was measured, and a maximum 14-fold enhancement in the diffusion coefficient of dye

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at a nanoparticle volume fraction of 0.5% was observed. Pineda et al. (2012) and Lee et al. (2011) investigated the CO₂ absorption enhancement by methanol-based Al₂O₃ and SiO₂ nanofluids, and a significant increase of the absorption rates in Al₂O₃ and SiO₂ nanofluids was observed. Kim et al. (2008) developed silica nanofluids in water for application in CO₂ absorption, and their results showed a 79% increase of CO₂ absorption rate in a bubble absorber. A survey of convective mass transfer of silica electrolyte nanofluid was experimentally conducted in a horizontal circular tube by Keshishian et al. (2013), and an increase of the mass transfer coefficient up to 20.94% was observed at a Reynolds number of 326. Sara et al. (2011) employed the electrochemical limiting diffusion current technique (ELDCT) with a rotating disc electrode (RDE) to measure the mass transfer coefficient in CuO/ferri-ferrocyanide nanofluid. Their results showed a 50% enhancement in the mass transfer rate in the nanofluid at the highest solid concentration of 1.94 vol%. Also employing ELDCT, the mass transfer coefficient was measured by Beiki et al. (2013) in a γ -Al₂O₃/electrolyte nanofluid in a straight tube. Their results indicated that a maximum augmentation of the mass transfer rate of 16.8% occurred for a 0.01% volume fraction of alumina nanoparticles at a Reynolds number of 1260. Fang et al. (2009) found that the diffusion coefficient of Rhodamine B in Cu-water nanofluid with a 0.5% Cu nanoparticle volume fraction was 26 times greater than that in the base fluid at 25°C.

The basic mechanism(s) for the mass transfer enhancement by nanoparticles are still not very clear now. Kim et al. (2006) investigated the effect of nanoparticles on bubble absorption by experiment and found that the addition of nanoparticles enhanced the absorption performance up to 3.21 times in a NH₃/H₂O system. They explained the enhancement of nanoparticles on mass transfer according to the grazing effect. The enhancement of the mass transfer characteristics for a NH₃/H₂O bubble absorption process using a CNTs-ammonia binary nanofluid was investigated by Ma et al. (2009). The results show that the mass fraction of CNTs had an optimum value for the effective absorption ratio of the binary nanofluid. They analyzed the mechanisms of the enhancement of bubble absorption in nanofluids from four possible factors: micro-convection, grazing effect, increase in gas holdup and the synergy of heat and mass transfer. By assuming that the Brownian motion of suspended nanoparticles and induced microscopic convection of fluids around the nanoparticles are the most important factors for the enhancement of mass transport, Xuan (2009) applied two approaches, the Green-Kubo principle and the heat and mass transfer analogy for finding the effective mass diffusivity in nanofluids. Veilleux and Coulombe (2011) presented a Brownian motion-induced dispersion model of mass diffusion in nanofluids, following an analysis of the velocity autocorrelation function decay. The model

showed a strong dependence on the mass transfer Péclet number and justified the order of magnitude differences between the mass diffusivity and thermal conductivity enhancements reported in the literature.

In the present study, nanofluids with carbon nanotube (CNT) nanoparticles in deionized water (nanofluid) were produced and the enhancement performance for CO₂ absorption investigated. The effect of parameters such as the solids concentration, stirring speed, ultrasonic time and the surface treatment of the CNT were examined experimentally. The mechanism for the enhancement of mass transfer was discussed in detail.

MATERIALS AND METHODS

Nanofluid preparation

Deionized water and CNT (MWNT, 10~20 nm in diameter, ~5 μ m in length and a specific surface area of 332 m²/g) were used to produce nanofluids. CNTs were provided by Beijing Dk Nanotechnology Co., LTD., China. It is known that CNTs have a hydrophobic surface, which is prone to aggregation and precipitation in water in the absence of a dispersant/surfactant (Nasiri et al., 2012; Tanshen et al., 2013; Ghozatloo et al., 2014; Talaei et al., 2011). For better dispersion, MWCNTs were made polar by chemical treatment in this work.

The chemical treatment of CNTs involved adding CNTs into HNO₃ solution with a concentration of 65% (wt) in a flask equipped with a reflux condenser. The suspensions were stirred and refluxed at 85°C for 1~7 h, and then naturally cooled down to room temperature. MWNTs were filtered from the acid solution and washed with deionized water until the pH of the MWNTs reached around 7. The soaked MWNTs were then dried in a vacuum oven at 40 °C for 24 h. The parameters such as the acidification time and the mass ratio (*R*) of CNT to the solution of 65% HNO₃ were varied to study the effect of the acid treatment on the stability of the nanofluids and the enhancement of CO₂ absorption.

For the purpose of preparing the required nanofluids, the CNTs were added to deionized water and then agitated by a TS-800 ultrasonic vibrator (Beijing Tense Technology Co. Ltd., China) for 0-3 hours at a frequency of 40 kHz and an output power of 100 W.

Characterization method

Fourier transform infrared spectroscopy (FTIR, TENSOR 37, from BRUKER OPTICS, Germany) was employed to analyze the surface of the CNTs after functionalization. For the FT-IR, CNTs were pressed into a pellet and scanned from 500 to 4000 cm⁻¹ with a resolution of 4 cm⁻¹. The dispersion stability of the CNT nanofluids

was measured with a UV-visible spectrometer (UV-1800, Shimadzu, Tokyo, Japan) in the wavelength range from 200 to 600 nm and by observation through transmission electron microscopy (TEM, X-650, from Hitachi, Ltd., Japan).

Absorption Experimental setup and procedures

Fig. 1 shows the schematic diagram of the absorption experimental equipment. The absorption experiments were carried out in a thermostatic stainless steel reactor with the volume of 1L. The inner diameter of the reactor was 80 mm and the height 250 mm. A propeller agitator was employed. Two impellers with diameters of 30 mm were installed on the same shaft to mix gas and liquid phases, respectively; each had three blades. A cooling coil in the vessel was connected to the thermostatic bath to maintain a constant reaction temperature (298 ± 0.1 K). Vessel 2 was a reference vessel, and a pressure difference transducer 11 was connected between vessel 2 and reactor 8 to indicate the growing pressure difference due to the absorption of CO₂ in the reactor.

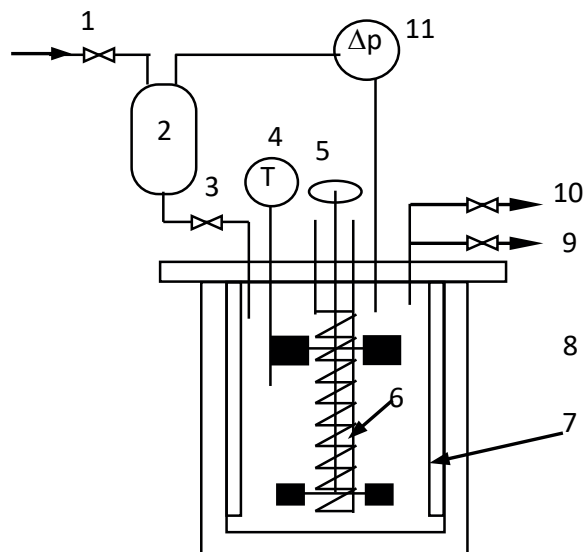


Figure 1. Experimental set-up for gas absorption 1–air inlet valve; 2–balance tank; 2–junction valve; 4–temperature sensor; 5–magnetic stirrer; 6–cooling coil; 7–baffles; 8–stainless steel reactor; 9–gas outlet; 10–vacuum; 11–pressure difference transmitter (connected with the computer).

Before each experiment, about 0.4 L of liquid was added into the reactor 8. The liquid was vacuum-degassed by opening valve 10, until the slurry was equilibrated under the water vapor pressure, then valve 10 was closed, whereafter valves 1 and 3 were opened and CO₂ in the gas cylinder was fed in up to a fixed pressure. Valves 1 and 3 were then closed rapidly, and the absorption started. The initial pressure of 0.1 MPa was used in the experiments.

The pressure drop due to the absorption was recorded by the transducer every 30s and transmitted to the computer. With this, the absorption rate can be calculated. All absorption experiments were repeated in triplicate. The experimental errors were calculated and the results were expressed as means and standard deviation in the Figures.

A typical variation curve of pressure difference with time is shown in Fig. 2. The slope of the curve at a given time is proportional to the absorption rate at that point of time. To illustrate the enhancement characteristics of nanofluids, the experimental enhancement factor E is defined as the ratio of the initial absorption rate with and without solid particles added, and the initial absorption rate can be calculated according to the slope of the $\Delta p-t$ curve obtained at $t=0$. If E is larger than 1.0, it can be said that the nanofluid enhances the absorption performance. If it is less than 1.0, the nanofluid has a negative effect on the absorption performance.

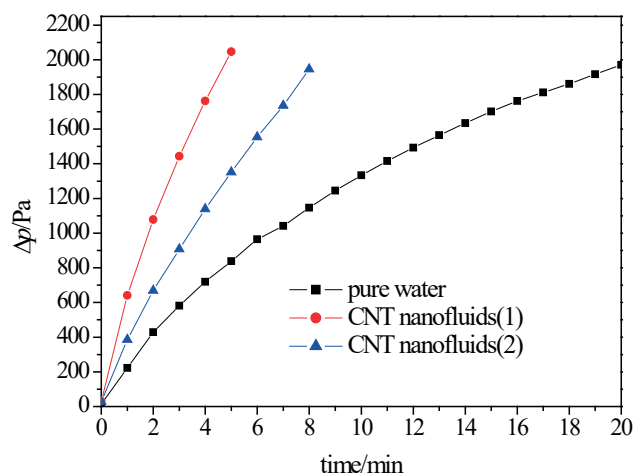


Figure 2. Pressure difference of CO₂ with batch time in pure water and nanofluids with CNT mass fraction of 0.01% and ultrasonic time of 2hr at no stirring CNT nanofluids (1): R= 140, nitration time=5hr; CNT nanofluids (2): R= 46.67, nitration time=5hr.

RESULTS AND DISCUSSION

Stability of the nanofluids

Some research showed that there is a good corresponding relation between the stability of nanofluids and the thermal conductivity (Wang et al., 2009; Zhu et al., 2009). However, few studies were carried out about the effect of the dispersion of nanofluids on mass transfer. In this work, the stability of the samples was investigated first because of its importance.

The surface treatment of CNTs can increase the hydrophilic groups in their structure and improve the dispersibility of CNT suspensions (Munkhbayar et al.,

2012; Munkhbayer et al., 2012). The FT-IR spectra of functionalized CNTs with different mass ratios of nitric acid to CNT and different nitration times are depicted in Fig. 3 and Fig. 4, respectively. The detectable transmission bands around 3420 and 1060 cm^{-1} are attributed to the presence of hydroxyl groups (-OH). However, the bands near 1600 cm^{-1} are well linked to the C=O stretching vibrations of carboxylic groups (-COOH) and extra peaks around 800 cm^{-1} can be assigned to the stretching vibration of C-O-C groups (Ghozatloo et al., 2014; Liu et al., 2005; Nasiri et al., 2011). The FT-IR results clearly show that the hydrophilic groups such as hydroxyls and carboxylates have been introduced onto the treated CNTs surfaces. With increasing ratio of nitric acid to CNT and nitration time, the peaks become more acute, which indicates an increase in the amount of hydrophilic groups.

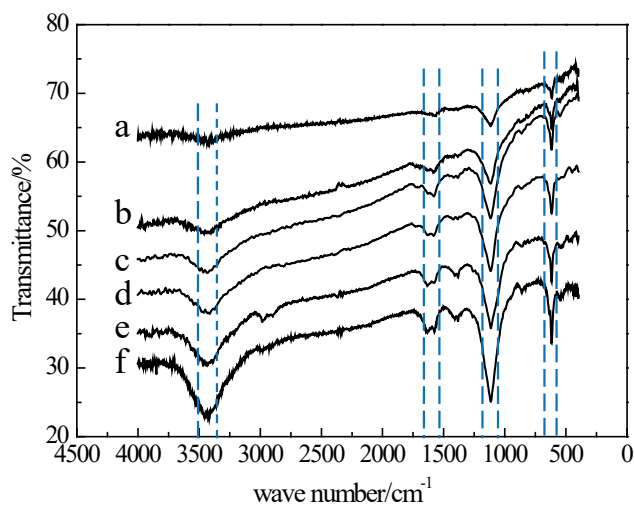


Figure 3. FT-IR spectra of CNT under 5 hours of nitration with different mass ratio R of nitric acid to CNT: a. raw CNT; b. R=46.67; c. R=93.33; d. R=140; e. R=186.67; f. R=233.33

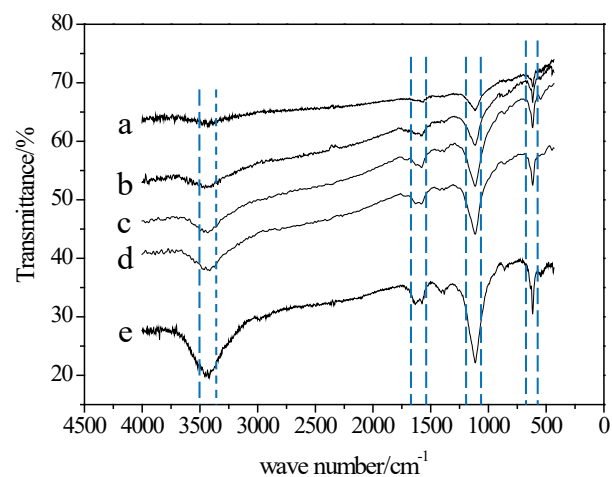


Figure 4. FT-IR spectra of CNT under different nitration times with the mass ratio of nitric acid to CNT of 140: a. raw CNT; b. 1hr; c. 3hr; d. 5hr; e. 7hr

The CNTs functionalized with hydroxyl groups can be dispersed well in water. The dispersibility of carbon nanotubes can be characterized using UV-vis absorption spectroscopy, and higher absorbance indicates better dispersion and solubility of the CNTs in solution (Nasiri et al., 2012; Munkhbayer et al., 2012; Karami et al., 2014). UV-vis spectra of the functional CNT nanofluids under different nitration times and different mass ratios of nitric acid to CNTs are shown in Fig. 5 and Fig. 6, respectively.

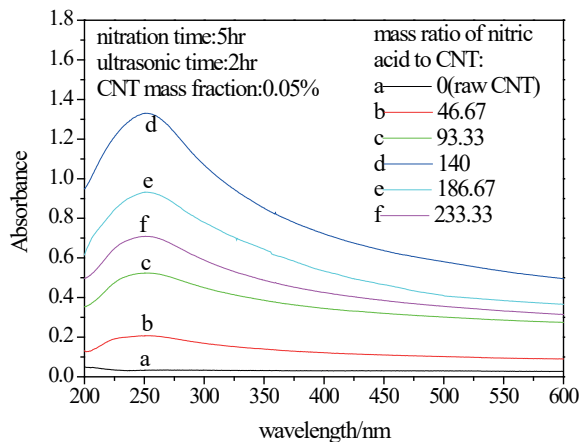


Figure 5. UV-vis spectra of CNT nanofluids prepared at different mass ratio of nitric acid to CNT.

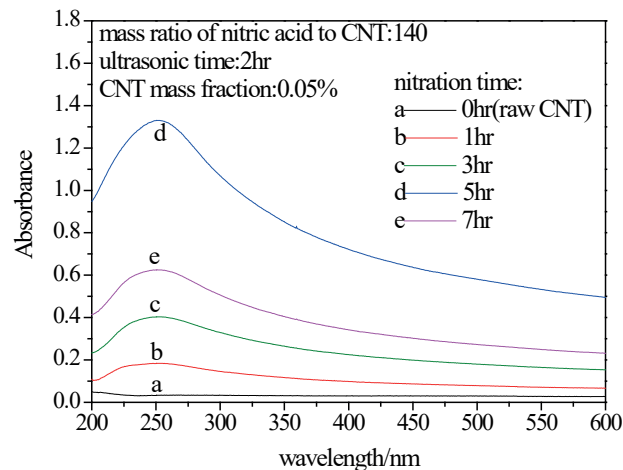


Figure 6. UV-vis spectra of CNT nanofluids prepared with different nitration times

From the figures, the peak absorbance of the samples is around 250 nm. The smallest absorbance was observed for the dispersion of raw CNTs, despite the application of ultrasonication, indicating the poor dispersion of raw CNTs in aqueous solution. After the acid treatment, the presence of hydrophilic groups (e.g., hydroxyl, epoxy, or carboxyl) on the surface of CNTs improves the dispersibility of the CNT suspension greatly and the absorbance increases rapidly. However, the absorbance does not continue to increase or maintain with the increase of nitration time and the ratio of nitric acid to CNT; thus, the absorbance

decreases when the nitration time is longer than 5 hour and the ratio of nitric acid to CNT is larger than 140. Too long of a nitration time and too large an amount of nitric acid may induce excessive nitrification of CNTs, resulting in the degradation of the carbon nanotubes. Fig. 7(a)–(c) shows the pictures of raw CNT and treated CNTs at different nitration time with a mass ratio of nitric acid to CNT of 140 using the wet-TEM technique. Entanglement and agglomeration can be observed for raw CNTs. After

acidating for 1 hour, the carbon nanotubes somewhat unfold, and when the acidification time is over 7 hour, some cracked nanotubes can be found and the length of the carbon nanotubes gets shorter. Though the images are not entirely representative of all nanofluid samples, they give a good indication of the damage caused by excessive acidification. Too small nanotubes agglomerate more easily due to too intense Brownian motion.

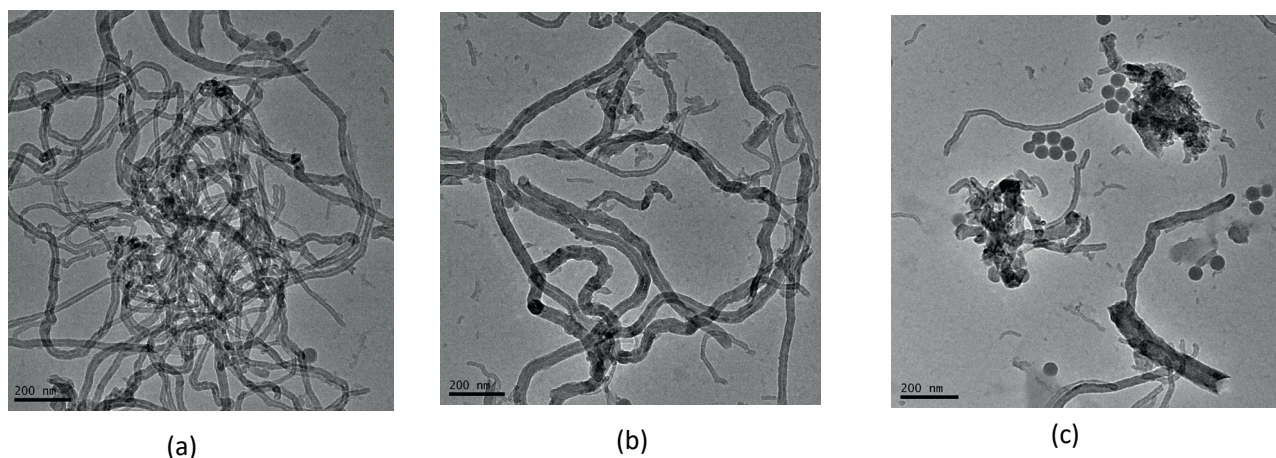


Figure 7. Wet-TEM images of aqueous suspensions of 0.01 wt% CNT (a) raw CNT; (b) the ratio of nitric acid to CNT of 140 at a nitration time of 1 hour and (c) the ratio of nitric acid to CNT of 140 at a nitration time of 7 hour .

The sonication time is also an important parameter for dispersing the aggregated nanoparticles (Li et al., 2007; Yousefi et al., 2012). Fig. 8 depicts the UV-spectra of CNT suspensions prepared with different ultrasonic times. With the increase of ultrasonic time, the absorbance increases rapidly, but when the time is longer than 2 hours, a decline of the absorbance was observed. The nanofluid stability was impacted by the stronger cavitation effect of ultrasonic vibration. The proper ultrasonic vibration can promote a fully dispersed and more stable nanofluid. But if the time of ultrasonic vibration exceeds the optimal ultrasonic time, with the increase of solution temperature, the nanoparticles accelerate, which induces the collision of nanoparticles and the nanofluids aggregate again.

The effect of stirring speed and CNT concentration on CO₂ absorption enhancement

The enhancement factor E for nanofluids with different stirring speeds and different solid concentrations is shown in Fig. 9, in which curves a, b and c are for CNT nanofluids prepared by ultrasonic vibrating for 2 hour, and curves d, e and f are for CNT suspensions without any ultrasonic vibration. The CNT particles were treated with nitric acid for 5 hours at the mass ratio of nitric acid to CNT of 140. As shown in Fig. 9, for all cases of CNT suspensions and at all stirring speeds, the enhancement factor E starts to increase

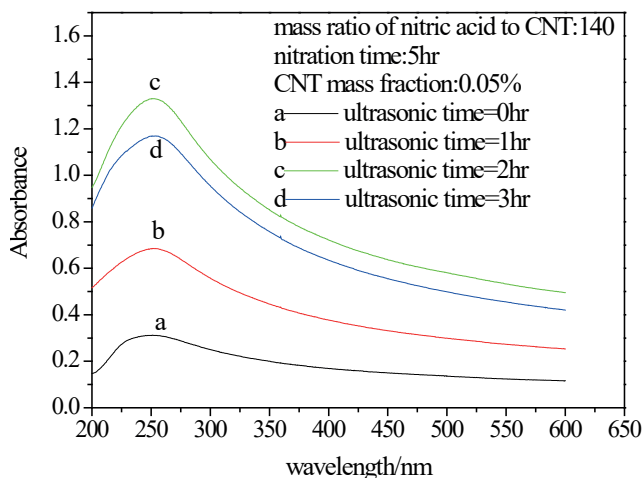


Figure 8. UV-vis spectra of CNTs nanofluids prepared when different ultrasonic times

rapidly with the increase of CNT concentration, and then levels off after a certain value of the CNT concentration (mostly 0.08% (wt) in the present experiments). For both suspensions with or without ultrasonic vibration, the enhancement factor decreases with the increase of agitation speed. However, the enhancement factor for CNT nanofluids with 2 hour ultrasonic agitation is obviously higher than that without sonication.

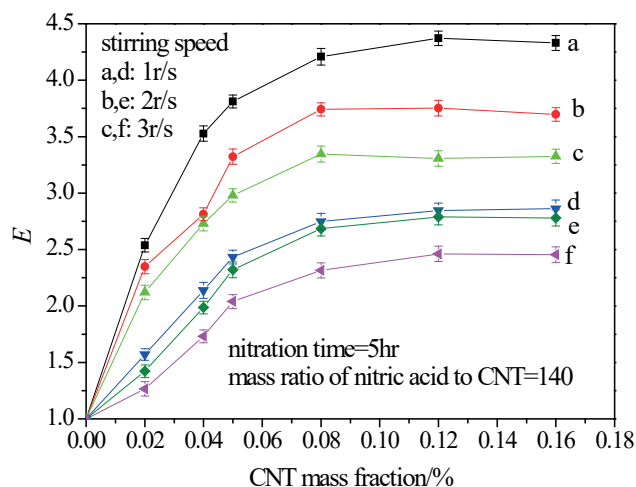


Figure 9. The effect of stirring speed on the enhancement of CO_2 absorption by CNT after chemical treatment with a, b, c: CNT nanofluids with ultrasonic time of 2 hr, and d, e, f: CNT addition without ultrasonic vibration.

As a comparison, the absorption improvement in raw CNT suspensions without ultrasonic vibration is shown in Fig. 10. The absorption of CO_2 can also be strengthened by raw CNT, but the enhancement factor is less than that in functionalized CNT suspensions. Furthermore, the variation trends of the enhancement factor for the raw CNTs are different for the functional CNTs. The enhancement factor E for raw CNT suspensions initially increased, but when the stirring speed is beyond 3 r/s the enhancement factor did not increase further.

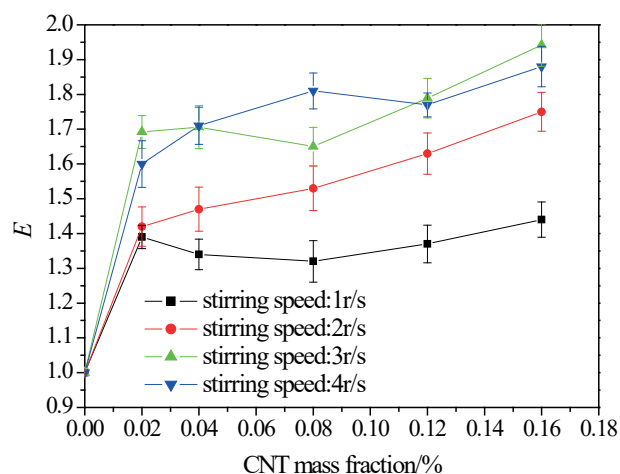


Figure 10. The effect of stirring speed on the enhancement of CO_2 absorption for raw CNT suspensions without vibration

The mechanism that explains such mass transfer enhancement is still speculative. The synergistic effect of

heat and mass transfer was proposed by Ma et al. (2009). They investigated the absorption enhancement for a $\text{NH}_3/\text{H}_2\text{O}$ bubble absorption process using a CNT-ammonia binary nanofluid, and suggested that the improvement of heat transfer can decrease the temperature at the gas-liquid interface and heighten the absorption potential of NH_3 . However, in this study, the absorption of CO_2 in water is exothermic, so the enhancement of mass transfer should not be attributed to the temperature variation at the gas-liquid interface. Kim et al. (2014) developed the hydrodynamic effect mechanism, in which the nanoparticles surrounding the bubbles break the diffusion boundary layer and make it thinner. Diffusion into the liquid film is increased by the presence of the particles near the interface between the bubble and the liquid. Pineda et al. (2012) suggested the bubble breaking model, in which the nanoparticles suspended in the base fluid cover the bubble, and as the movement of the fluid due to external forces become more dynamic, the particles collide with the gas-liquid interface, breaking the bubble into smaller size bubbles. More bubbles mean a larger interfacial area, which would promote the mass transfer from the gas to the liquid. However, the hydrodynamic effect mechanism and the bubble breaking model are developed mainly for bubble systems (bubble columns, sparged stirred tanks).

For gas absorption in a reactor with a flat interface employed in this work, the shuttle effect and the micro-convection caused by the Brownian motion of the nanometer particles are believed to play more dominant roles in the mass transfer enhancement (Manikandan et al., 2012; Zhu et al., 2008; Nagy et al., 2007). The shuttle mechanism is based on the notion that the particles adsorb an additional amount of the absorbed gas at the gas-liquid interface or within the liquid film, after which this adsorbed gas desorbs from the particles into the bulk liquid. With this so-called "shuttle" between the interface and the bulk, the gas absorption rate is enhanced (Kim et al., 2006; Kim et al., 2007). For very small size particles, the Brownian motion cannot be neglected, which causes a velocity disturbance field in the fluid (Krishnamurthy et al., 2006; Nagy et al., 2007; Kluymans et al., 2002). According to Nagy et al. (2007), even at very small values of particle concentration, the flow field around nanoparticles will interact, and this can create increased momentum transport according to increased velocity gradients in the boundary layer of the nanosized particles; consequently, it can increase the mass transport in the nanofluid.

According to Dagaonkar et al. (2003), the particles which intensify mass transfer by the grazing effect should be adsorptive and hydrophobic. Raw CNT particles have a large amount of hydrophobic groups on the surface and show a good selective adsorption of CO_2 (Policicchio et al., 2015; Surapathi et al., 2013). Sun et al. (2008) measured the sorption/desorption isotherms of CO_2 on MWCNTs in the presence of water. Their results show that, even at a

high ratio of H₂O/CO₂, a good adsorbability of CNTs to CO₂ is still retained. However, the hydrophobic groups on the surface also induce the agglomeration of CNT particles easily, and weakening the effect of the micro-convection caused by the Brownian motion. Therefore, we hold that the enhancement of CO₂ absorption by the raw CNTs should be mainly attributed to the shuttle effect. For CNTs under acid treatment, the adsorption ability of CNTs to CO₂ is lowered greatly compared to the raw nanotubes (Policicchio et al., 2015; Surapathi et al., 2013). Hydrophilic groups such as hydroxyls and carboxylates introduced onto the treated CNTs surfaces interact readily with water molecules. These surface active sites of CNTs are easily covered by water molecules, resulting in a further decrease in the adsorption capacity of CNTs to CO₂ in aqueous solution. The influence of the micro-convection caused by the Brownian motion is hence strengthened. Especially for stable nanofluids under 2 hour ultrasonic agitation, the micro-convection may play the main role for the enhancement of CO₂ absorption. A combination of the micro-convection and the grazing effect can be used to explain the increase of the CO₂ absorption rate in suspensions of functional CNTs without ultrasonic agitation.

From Fig. 9 and Fig. 10, a different variation of the enhancement factor with stirring speed can be found for treated CNTs and raw CNTs, respectively. For raw CNTs, the enhancement factor initially increased with stirring speed, and when the agitating speed was higher than 3 r/s, no further increase was observed, while in treated CNTs suspensions (with or without ultrasonic agitation), the enhancement factor decreased monotonously with increasing stirring speed.

The influence of stirring on mass transfer enhancement can be analyzed from several aspects. Firstly, high speed stirring effectively prevents the agglomeration and precipitation and the particles can be well dispersed in the slurry, which is advantageous for the absorption enhancement. Second, agitating in the absorption process can increase the absorption rate greatly and thus weaken the enhancement effect caused by the nanoparticles.

For raw CNTs which are easily agglomerated in suspensions, stirring can disperse the particles in the base fluid effectively, and hence the enhancement factor at low stirring speeds (such as 1 r/s) was less than that at high speeds. When the agitation speed was higher than 3 r/s, the increase of absorption rate caused by the agitation plays a prominent role gradually, the enhancement by the nanoparticles is weakened. (Fig. 10). However, for the functional CNTs, which have large amount of hydrophilic groups on the surface, the solid particles more easily disperse in water and the effect of agglomeration inhibition by stirring is small. Thus, with increasing stirring speed, the role of “shuttle” and micro-convection is weakened, resulting in a decrease of the enhancement factor, as shown in Fig. 9.

The influence of the concentration of CNT nanoparticles is also shown in Fig. 9 and Fig. 10. When the particle concentration reaches a critical value, a gradual leveling off of the enhancement factor takes place. This behavior can be explained from several aspects. (1) The decrease of the self-diffusion coefficient (Pineda et al., 2012; Gerardi et al., 2009). The tortuosity of the diffusion path of the solute molecules is increased when solid particles stand in their way. When the particle concentration surpasses a critical value, the nanoparticles will become too dense in the liquid phase, reducing the self-diffusion coefficient and consequently reducing the absorption of the gas phase. (2) For hydrophobic particles, with increased the loading of solid particles, the coverage of the particles at the gas-liquid interface has a maximum value (Dagaonkar et al., 2003; Brilman et al., 1998), and thus the increase of the absorption rate also reaches an asymptotic value. This is more appropriate for the explanation of the absorption enhancement by raw CNT.

Another phenomenon, observed from Fig. 9, is that the enhancement factor for CNT nanofluids under 2 hour ultrasonic agitation is obviously higher than that without sonication, is related to the stability of the nanofluid. The influence of ultrasonic time on the enhancement factor can be further demonstrated from Fig. 11. When the ultrasonic time increases from 1 hour to 2 hour, the enhancement factor increases rapidly. At an ultrasonic time of 2 hours, the maximum enhancement factor reaches about 4.9. However, the absorption enhancement by the nanofluid with ultrasonic vibration does not strengthen or maintain with the increase in time; it can be seen that the enhancement factor decreases when the time is longer than 2 hour. This variation of the enhancement factor corresponding to the stability of nanofluids under different ultrasonic times is shown in Fig. 8. The excess sonication

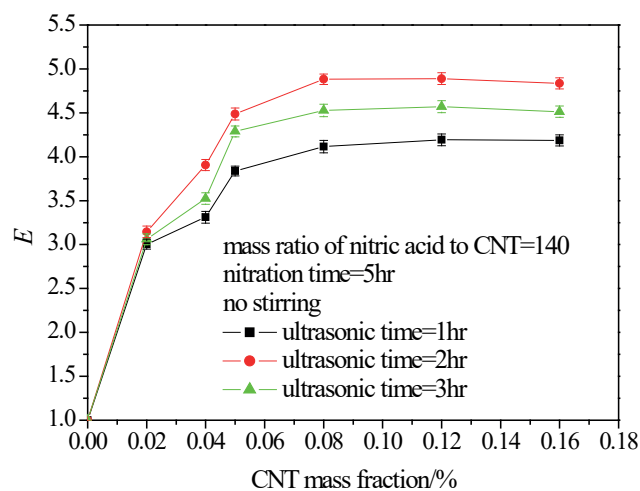


Figure 11. The effect of ultrasonic irradiation time on the enhancement of CO₂ absorption for CNT nanofluids with no stirring.

may induce a cavitation effect, leading to the collision of nanoparticles and the nanofluids become unstable again. From Yang et al. (2011), some superior properties of the nanofluid, such as micro-convection and the high heat and mass transfer coefficient, cannot be fully functional when the nanofluid is poorly stabilized.

The effect of chemical treatment on CO₂ absorption enhancement

The aim of acid treatment of CNTs is to increase the hydrophilic groups on the surface of CNT particles and improve the stability of the nanofluids. However, the chemical treatment may change the structure of CNTs and have an effect on the absorption enhancement performance of nanofluids. The effect of nitrification time and of the amount of nitric acid on the enhancement factor was investigated, as shown in Fig. 12. With lengthening acidification time and increasing amount of nitric acid, a similar variation was observed: the enhancement factor first increased and then decreased. The maximum enhancement factor was found at a nitration time of 5 hour and mass ratio of nitric acid to CNT of 140.

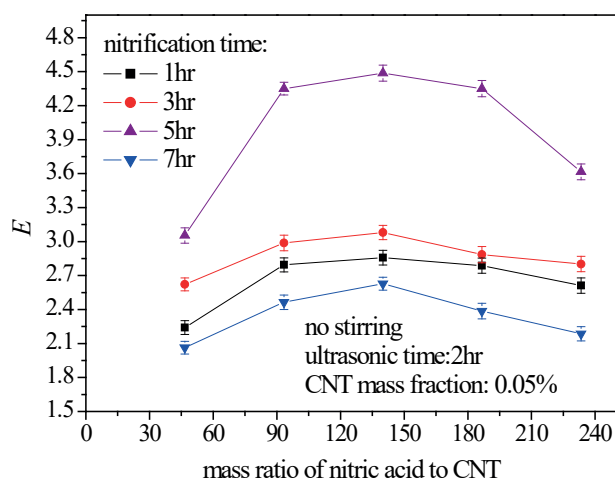


Figure 12. The effect of the amount of nitric acid and the nitration time of the CNT chemical treatment on the enhancement of CO₂ absorption

The effect of chemical treatment can be demonstrated from two aspects. Firstly, different dispersion performance of CNT nanofluids can be obtained under different operating conditions for acid treatment. From Fig. 5 and Fig. 6, lengthening the acidification time and increasing the amount of nitric acid make the nanofluids more stable. But when the nitration time is longer than 5 hour and the ratio of nitric acid to CNT is larger than 140, the nanoparticles agglomerate easily again. This stability variation of CNT nanofluids corresponds to the change in the enhancement factor with nitration time and the amount of nitric acid.

Secondly, the decrease of hydrophobic groups on the surface due to the acid treatment leads to the reduction of the adsorption capacity for the solute. The improvement of the absorption rate by the shuttle effect is decreased greatly.

CONCLUSIONS

In this study, the dispersion stability is evaluated for CNT nanofluids for different acidification times, amount of nitric acid and ultrasonic irradiation time. Experiments of CO₂ absorption enhancement by CNT suspensions were carried out. The following conclusions are drawn from the present work.

(1) Through nitric acid treatment, hydrophilic groups were introduced onto the surface of CNTs particles and improve the stability of CNT nanofluids. The experimental results showed that a 5 hour nitrification time and mass ratio of nitric acid to CNT of 140 were recommended for good dispersion stability of CNT nanofluids.

(2) It is found that the CO₂ absorption rate can be enhanced in suspensions of raw CNTs and functionalized CNTs. However, the variation of the enhancement factor with stirring speed is different. For raw CNTs, the enhancement factor increases, but when the stirring speed is beyond 3 r/s, the enhancement factor does not increase further; for functionalized CNTs, the enhancement factor decreased monotonously with the agitation speed.

(3) The increase of absorption rate is influenced by the stability of the nanofluids. The enhancement factor is obviously higher in CNT suspensions with 2 hour sonication than without any ultrasonic agitation, and there is an optimal ultrasonic time for better enhancement of CO₂ absorption.

(4) Acid treatment of CNTs improves the absorption performance of nanofluids greatly. The acidification time of 5 hour and the mass ratio of nitric acid to CNT of 140 are recommended as the optimum nitrification conditions.

(5) The mechanism was discussed based on the experimental phenomena, and we hold that the micro-convection caused by Brownian motion and the shuttle effect are more plausible to explain the mass transfer enhancement in CNT nanofluids.

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