Preparation of Graphene-amine Nanofluid for Absorption of Carbon Dioxide (CO$_2$) and Hydrogen Sulfide (H$_2$S) from a Natural Gas Stream in a Wetted Wall Column

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Abstract
How CO$_2$ and H$_2$S are removed from a natural gas stream, through a nanofluid containing nanoporous graphene in Diethanolamine (DEA) is revealed. The appropriate values are chosen for the nanosheet dosage and the liquid and gas flow rates to be applied in the absorption experiments. These experiments are run in a laboratory scale wetted wall column. The nanosheet concentration is within 0.005 to 0.5 wt % range. The surfactants and ultrasonic treatment is administered to prepare stable nano-fluids. It is found that applying nanoporous graphene in DEA has a significant affect on CO$_2$ and H$_2$S absorption in comparison with DEA. The absolute zeta potential values of nanofluids are greater than +35 mV. The effect of different parameters including nanosheet, CO$_2$ and H$_2$S concentrations, in the feed gas stream (two different samples) on simultaneous absorption of H$_2$S and CO$_2$ from CO$_2$-H$_2$S-CH$_4$ gas mixture is studied. By processing sample #1, abstract i.e, an improvement in CO$_2$ absorption to 39% and H$_2$S absorption up to 9% is observed at 0.1 wt% of nanoporous graphene/DEA nanofluids.

Keywords
Nanofluid; Wetted Wall Column; Hydrogen Sulfide; Carbon Dioxide; Diethanolamine; Nanoporous Graphene

1. Introduction
Acid gas treatment is an important industrial process in removing acid gases like carbon dioxide (CO$_2$) and hydrogen sulfide (H$_2$S) from natural gas (Kohl & Nielsen, 1997; Marzouk, Al-Marzouqi, Teramoto, Abdullatif, & Ismail, 2012). This process is run in natural gas processing, biogenerated methane processing, petroleum refining, and synthesis gases treatment plants. Every natural gas source contains different volumes of CO$_2$ and H$_2$S. Considering a high cost of gas transferring process, and the decrease in the volume heating value, CO$_2$ should be removed. Moreover, H$_2$S should be eliminated because it is a toxic and very corrosive gas (Chou, 2003; Kane, Horvath, & Cayard, 1996; Lambert, Goodwin, Stefani, & Strosh, 2006). Based on the type and amount of acidic gas, different methods are applied in their sweetening process. Some examples include: absorption into physical or chemical solvents, adsorption onto activated carbon, cryogenic distillation, and separation with solid and liquid membranes (Leppin, 2004). The most extensively applied gas treatment for acidic gas absorption is aqueous solutions of alkanolamines, a common material for removing acid gases. Some of the common solvents consumed in gas sweetening are: Monoethanol Amine (MEA), Diglycol Amine (DGA), Diethanolamine (DEA), Diisopropanol...
Amine (DIPA) and Methyl diethanol Amine (MDEA) (Mandal & Bandyopadhyay, 2005).
Since the mass transfer resistance in the interfacial surface usually creates an obstacle for increasing the contact surface in various phases, different methods for decreasing this resistance should be applied. There exist methods like mechanical, chemical, acoustic (Fan & Cui, 2005) and electromagnetic (Xu, Bai, Fu, & Guo, 2005) to enhance mass and heat transfer. However, each one of these methods enhances mass transfer by mixing where the creation of the turbulence, have their own restrictions (Hozawa, Inoue, Sato, Tsukada, & Imaishi, 1991). Nanotechnology is very contributive in this respect (S.-W. Park, Choi, Kim, Lee, & Lee, 2008; S.-W. Park, Choi, Kim, & Lee, 2007; S. W. Park, B. S. Choi, & J. W. Lee, 2006). and gas sweetening as a mass transfer phenomenon, could apply nanotechnology. Nanofluids consumption has become one of the most appropriate heat and mass transfer media because of the improvements made in heat and mass transfer coefficients. Krishnamurthy et al (2006) where the first to observe that a dye diffuses faster in a nanofluid than in water, and explained that the Brownian motion of the nanoparticles induces convection in the nanofluids. The assessments on mass transfer of nanofluids can be divided into two main categories: the diffusion of coefficients and convective mass transfer coefficients.

To enhance the gas absorption rate, nanofluids are applied. Ashrafmansouri and Esfahany (2014) reviewed a comprehensive study on mass transfer by applying nanofluid. There is no exact mechanism to describe enhancement of mass transfer using nanofluids. Some mechanisms like: grazing effect or shuttle effect, reducing film thickness, Brownian motion, bubble breaking, hydrodynamic and reduction in surface tension, have been and are mentioned in the literature (Ashrafmansouri & Esfahany, 2014). There exist some studies on absorption of ammonia by (J.-K. Kim, Akisawa, Kashiwagi, & Kang, 2007; J. K. Lee, Koo, Hong, & Kang, 2010; Ma, Su, Chen, Bai, & Han, 2009; Pang, Wu, Sheng, Zhang, & Kang, 2012; Yang, Du, Niu, Cheng, & Jiang, 2011) on carbon dioxide by (W.-g. Kim, Kang, Jung, & Kim, 2008; J. W. Lee, Jung, Lee, & Kang, 2011; S.-W. Park, B.-S. Choi, & J.-W. Lee, 2006; S. W. Park, Lee, Choi, & Lee, 2006; Pineda, Lee, Jung, & Kang, 2012)and on oxygen by (Nagy, Peczko, & Koroknai, 2007; Olle et al., 2006) all concerned with the effects of applying nanoparticles. The absorption rate of NH₃ in nanofluid of Cu, CuO, and Al₂O₃ of 50 nm size in water as base fluid is measured by Kim et al. (J.-K. Kim, Jung, & Kang, 2006) through a bubble absorber. Rene et al. (Rene, Veiga, & Kennes, 2012) reviewed several industrial techniques for waste gas treatment and H₂S removal from gas streams (including adsorption, absorption etc.), and concluded that the biological waste-gas treatment apparatus have a great potential in removing pollutants under 5 g/m³ by up to 90% efficiency. Physicochemical gas cleaning process would be an appropriate substitute for the cases where no filtration is possible. consuming nanofluids in removing H₂S as an absorbent is still a gap in this area. Esmaeili Faraj et al. Esmaeili (2014) performed an experimental study to find out the mass transfer rate on H₂S absorption through two different nanofluids, the silica and exfoliated graphene oxide (EGO) nanoparticles in water in a bubble column and revealed that consuming silica nanoparticles decrease the H₂S absorption. On the contrary, they mentioned that EGO-water nanofluid increases the H₂S absorption. Komati and Suresh (2008) applied a wetted wall column to study the absorption process in CO₂/ MDEA solution by a nanoferrofluid and revealed that the enhancement in mass transfer coefficient was 92.8% for a magnetite dosage of about 0.39 vol%.
Kim et al. (2008) assessed CO₂ absorption rate in a bubble type absorber by applying suspensions of SiO₂ nanoparticles in water. The nanoparticle dosage within was 0.01 wt. % to 0.04 wt. % range and they discovered that at 0.21 wt. %. It is reported that in case the nanoparticle dosage the CO₂ absorption increased by 24%.
Lee et al. (2011) applied a bubble type absorber to study the CO₂ removal by consuming methanol-based fluids. Their nanofluids contained Al₂O₃ and SiO₂ nanoparticles. The experiments were run subject to different dosages. They reported that the maximum CO₂ absorptions occurred at the following two states: a) 4.5% at 0.01 vol % of Al₂O₃ at 20°C and b) 5.6 % at 0.01 vol % of SiO₂ at -20°C in comparison with when pure methanol is consumed.
Park et al. (2006) studied the impact of consuming colloidal silica (0-31 wt %) / 2-amino-2-methyl-1-propanol on CO₂ absorption they in a stirred vessel. Their finding indicated that an increase in nanoparticle concentration would cause a decrease in the volumetric liquid-side mass transfer coefficient and the absorption rate in the nanofluid.
There exist other studies in the literature like (B.-J. Hwang, Park, Park, Oh, & Kim, 2009; S.-W. Park et al., 2008; S.-W. Park et al., 2007; S. W. Park, B. S. Choi, et al., 2006) where the impact of consuming SiO\textsubscript{2} nanoparticles in CO\textsubscript{2} removal in stirred cells are assessed. These experiments are run in aqueous solutions of DEA, MEA and DIPA. It is reported that an increase in the nanoparticle concentration leads to a decrease in CO\textsubscript{2} absorption rate due to the elasticity of the solution (Komati & Suresh, 2008).

By consuming Al\textsubscript{2}O\textsubscript{3} and SiO\textsubscript{2} nanoparticles in methanol based nanofluids, Pineda et al. (2012) conducted an experimental study to remove CO\textsubscript{2} in a tray column absorber, the nanoparticle dosage in this setup was 0.005-0.1 vol %. In comparison to pure methanol as the base fluid/absorbent, they observed an increase of 9.4% and 9.7% in CO\textsubscript{2} absorption rates in their experiments by consuming methanol-Al \textsubscript{2}O\textsubscript{3} and methanol-SiO\textsubscript{2} nanofluids, respectively. Jung et al. (2012) studied the CO\textsubscript{2} absorption by consuming Al\textsubscript{2}O\textsubscript{3}/methanol nanofluids. They found that the improvement of absorption rate with respect to the pure methanol was 8.3 % at 0.01 vol % of alumina nanoparticles, while the dosages of nanoparticles were between 0.005 to 0.1 vol %.

Taheri et al. (2016) studied simultaneous absorption of CO\textsubscript{2} and H\textsubscript{2}S from CO\textsubscript{2}-H\textsubscript{2}S-CH\textsubscript{4} gas mixtures containing DEA-based nanofluids in a wetted wall column. They reported that Al\textsubscript{2}O\textsubscript{3}-DEA nanofluid with 0.1 wt % nanoparticle increased the H\textsubscript{2}S mass transfer up to 14 % with respect to the base fluid like DEA. Moreover, it was revealed that by consuming SiO\textsubscript{2}-DEA nanofluid, H\textsubscript{2}S absorption decreased with respect to CO\textsubscript{2}, obtained results indicating a 33% and 44% improvement in Al\textsubscript{2}O\textsubscript{3}-DEA and SiO\textsubscript{2}-DEA nanofluids, respectively.

The usage of graphene has increased in many studies and based on its wonderful properties, it is known as the “star” material (Cai et al., (2008) [Chen et al., 2011; Geim, 2009; Li, Cai, Colombo, & Ruoff, 2009; Lu, Huang, Nemchuk, & Ruoff, 1999; Lu, Yu, Huang, & Ruoff, 1999; Marcano et al., 2010; May, 1969; Novoselov et al., 2004; O’Neill, Khan, Nirmalraj, Boland, & Coleman, 2011]). Some studies have found that the nanoporous graphene has a high capacity in sorption crude oil and petroleum products, fats, alkanes, toluene, and the other organic solvents, without any further modification or treatment.

Consuming amine containing graphene to improve the acidic gas absorption is a major concern in this field, therefore the focus on this issue is the subject here. It is expected observe an increase in mass transfer due to the high surface area to volume of nanosheets ratio.

The main purpose of this research is to explore the consumption of DEA-based nanofluids in a wetted wall absorber to remove CO\textsubscript{2} and H\textsubscript{2}S from different compositions of natural gas stream in a simultaneous manner. So far, suspensions containing nanoporous graphene in DEA 10 wt % are produced and consumed as a nanofluid, furthermore, many experiments are run in order to determine the impact of nanosheets dosage and inlet concentrations in the CO\textsubscript{2} and H\textsubscript{2}S removal process from the natural gas stream.

2. Materials and Methods

2.1. Materials

Two gas mixture cylinders are used each containing 50 × 10^{-4}\% H\textsubscript{2}S and 3\% CO\textsubscript{2} (gas sample #1) and 30 × 10^{-4}\% H\textsubscript{2}S and 1\% CO\textsubscript{2} (gas sample #2) in balance of CH\textsubscript{4} as the inlet gas composition for this experimental setup. These gas samples are purchased from Tarkib Gas Alvand Co., Tehran, Iran. The compositions of the mentioned samples are the same as the ones consumed in Sarkhoon and Qeshm gas treating company plants. The other consumed material is 99.99 \% pure N\textsubscript{2} gas in a cylinder provided from Industrial Gasses, Shiraz, Iran. DEA solvents of 85 \% pure N\textsubscript{2} gas are purchased from Arak Petrochemical plant, Iran. The nanoporous graphene is supplied by the Research Institute of Petroleum Industry (RIPI), Iran, with characteristics tabulated in Table 1. Nanoporous graphene is prepared through a special chemical vapor deposition (CVD) method introduced by (Pourmand, et al., (2015). Cadmium sulfate is purchased from Merck Germany.

<table>
<thead>
<tr>
<th>Nanosheet</th>
<th>Surface area (m\textsuperscript{2}.g\textsuperscript{-1})</th>
<th>Pore volume (cm\textsuperscript{3}.g\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>nanoporous graphene</td>
<td>850</td>
<td>2.11</td>
</tr>
</tbody>
</table>
2.2. Experimental Setup

A wetted wall column (WWC) is designed and constructed to explore the improvement in the mass transfer of input acidic gas by nanofluids. The schematic of the design is shown in Fig.1 and the details of the wetted wall column is illustrated in Fig. (2).

Figure 1. Schematic Diagram of the Experimental Set up
Plexiglass is used in fabricating the body of the wetted wall column in order to make the flow of the falling film visible. The length and the outer diameter of the stainless steel tube are 3.15 and in\textquoteright\textfrac{3}{4}\textquotedbl", respectively. The tube is installed inside a concentric glass tube with 3/2 in diameter. This experimental setup consists of an absorber test section (wetted wall column), a storage tank, liquid and gas flow meters, pressure indicator (PI), and temperature indicator controller (TIC). This system contains both the main gas and liquid streams.

2.3. Absorption Experiments

2.3.1. Gas Stream

The liquid and the gas mixture (containing H_{2}S, CO_{2} and CH_{4}) pass through a water bath to be heated on their turn. Their temperatures are kept at the fixed value of 298 K by AUTONICS TC4S, K type, ±0.1°C temperature controller. The gas samples # 1 or # 2 is introduced from the bottom of WWC at 1.8 psig which is let out from the top. Using a GX-2012, RKI, type B, Serial No: 489010956 H_{2}S analyzer, the concentration of H_{2}S in the outlet gas is measured at 5 minutes intervals. The same procedure for CO_{2} is followed through a GC (Varian CP 3800, USA), (ASTM D1945). The H_{2}S is absorbed while passing through a bubbler filled with Cadmium sulfate. At the end, the H_{2}S free gas stream is directed to a hood.

2.3.2. Liquid Stream

Nanoporous graphene consumed in DEA 10 wt.% (as our nanofluids) and DEA 10 wt.% solution are consumed as the absorption solutions. These liquid are kept in a 10-liter tank, which are injected to the middle of WWC through a 5 psig N_{2} gas pressure. The whole process is maintained at 298 K, the liquid flow liquid to the column is controlled by a rotameter before entering the bottom of WWC. The absorbent liquid level rises through a stainless steel tube then it exits from the top of this tube and pours down as a film on the outside of the tube wall and then exits at the bottom. Simultaneously, gas contacted with this film counter-currently. The liquid flow rate in all tests is about0.7 cc/s. The rate of absorption is determined by measuring gas concentration at the inlet and the outlet and applying the material balance for gas phase. The procedure of preparing absorbents is as follows: first, the amine solution is prepared by mixing 10 wt.% DEA with de-ionized water and next this solution is titrated with standard HCl through using mixing indicator to determine the total amine concentration. The nanoporous graphene sample is prepared according to CVD method in a catalytic basis (Pourmand et al., 2015). During 5-30 minutes, the furnace's temperature rises to 900-1100 °C. The carbon source is the methane gas and its volume is four times the carrier gas volume, hydrogen. The metal nanocatalysts are removed from the product by stirring it in 18% HCl solution at room temperature for 16
In order to complete the purification process, the sample is rinsed with distilled water for a couple of times and finally dried at 100 °C. A high molecular and non-ionic surfactant named GA (Gum Arabic) is consumed as a dispersion stabilizer. The absorbent concentrations is within 0.005 to 0.5 wt% range. Moreover, the graphene’s weight basis is twice the dispersion stabilizer weight. Observing the good stability of nanoporous graphene/DEA nanofluid with GA is an indicator that Gum Arabic would be an appropriate additive for these nanofluids. The reason for the stabilization effect is the steric repulsive force caused by the adsorbed polymers. When two particles repulse, in case they get close to each other, the stability will be induced (Butt, Graf, & Kappl).

To disperse carbon nano materials in a base fluid, it is preferred to apply the two-step method. The nanosheets are provided by the Research Institute of Petroleum Industry (RIPI). Based on the samples’ composition and the nanosheet and surfactant ratio, the appropriate volume of nanosheets, surfactant and fluid are calculated and selected. The fluid is broken into two parts. The nanosheets is dispersed in part # 1, stirred and then put in an ultrasonic bath until the nanosheet dispersion process is completed. [The technical characteristics of the bath were Sonoswiss SW 12 H, power: 1000 watt, frequency: 38 kHz.] The surfactant is dissolved in part # 2 and the solvent is added to the suspension and kept in the ultrasonic bath for half an hour. [For each one of nanofluid particle, the distribution stability was tested for 24 hr.] The nanofluids are well distributed and the sedimentation is not observed for the present experimental conditions.

For production of nanofluids, stability is among the key aspects to be considered because of their suspension nature. Some procedures are applied to determine stability like: zeta potential, UV etc. (Amrollahi, Hamidi, & Rashidi, 2008; Yujin Hwang et al., 2008; Y. Hwang et al., 2007). One of the parameter/ procedure applied in determining the stability of nanofluids, is zeta potential. After the suspensions were stirred thoroughly and ultrasonicated for at least 20 min, 2-4 mL of suspensions are transferred into a measuring cell. Then zeta potential is measured by a Malvern ZS Nano S analyzer (Malvern Instrument Inc, London, UK). The measurement is taken at V=10 V, T=25°C with switch time at t=50s. Each experiment was repeated at least three times to calculate the mean value of the experimental data (Amrollahi, Rashidi, Emami Meibodi, & Kashefi, 2009). This parameter varies within -100 to +100 mV range. Zeta potential is a measure to calculate the electrostatic charge interactions of nanoparticles and ions in the fluid surfaces. The value of zeta potential greater than +25 mV or less than -25 mV vindicates an appropriate stability. At low zeta potential, the nanoparticles aggregate and make the fluids unstable (Talaei, Mahjoub, morad Rashidi, Amrollahi, & Meibodi, 2011). The experimental operating conditions are tabulated in Table 2. The surface morphologies are studied by the field-emission scanning electron microscopy (FEI Quanta 650F Environmental SEM) attached to an energy-dispersive X-ray spectroscopy (EDS) analyzer to measure the samples’ composition and transmission electron microscopy (Tecnai G2 F20 STWINHR(S) TEM, FEI).

**Table 2. Experimental Operation Conditions**

<table>
<thead>
<tr>
<th>Base fluid</th>
<th>Kinds of nanosheet</th>
<th>Concentration of nanosheets(wt% of nanosheets)</th>
<th>Gas flow rate (m³/s)</th>
<th>absorbent flow rate (m³/s)</th>
<th>Gas composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>DEA 10 wt%</td>
<td>...</td>
<td>9.33x10⁻⁶</td>
<td>0.7x10⁻⁶</td>
<td>Sample # 1, 2</td>
</tr>
<tr>
<td>2</td>
<td>DEA 10 wt% nanoporous graphene</td>
<td>0.005, 0.01, 0.05, 0.1, 0.5</td>
<td>9.33x10⁻⁶</td>
<td>0.7x10⁻⁶</td>
<td>Sample # 1, 2</td>
</tr>
</tbody>
</table>

*Sample # 1: Feed gas mixture composition, 50x10⁻⁴% H₂S and 3% CO₂ in balance of CH₄. Sample #2: Feed gas mixture composition, 30x10⁻⁴% H₂S and 1% CO₂ in balance of CH₄, Temperature = 298 K, system pressure = 1.8 psig*
3. Results and Discussion

3.1. Nanofluid Characterization and Dispersion Stability

Transmission Electron Microscopy (TEM) is a crucial characterization tool in direct imaging of nanomaterials and obtaining quantitative measures of particle and/or grain size, size distribution, and morphology. The HRTEM (High-resolution transmission electron microscopy) image of a crumpled and randomly oriented nanoporous graphene sample is shown in Fig. (3). As observed the size of the graphene sheets is about 40-50 nm, which increases the surface area; thus, the sorption capacity in comparison with other kinds of graphene (with nonporous sheets); obtained through other methods (Farghali, Bahgat, El Rouby, & Khedr, 2013; Geng et al., 2011; Seresht, Jahanshahi, Rashidi, & Ghoreyshi, 2013; Yuan, Li, & Li, 2011).

The SEM image of the graphene with its highly porous morphology is seen in Fig. (4). It should be noted that in the SEM image the macroporous ?? ?? are detectable and the smaller pore sizes (i.e. mesopore and micropore) are characterized using through BET analysis tabulated in Table 1.

Figure 3. HRTEM Image of Nanoporous Graphene

Figure 4. SEM Image of Nanoporous Graphene
As mentioned earlier, in this article, the zeta potential parameter is applied to measure the stability of the prepared nanofluids. It should be noted that zeta potential is the potential difference between the two layers of the stationary layer of fluid attached to the dispersed particle and the dispersion medium. The zeta potential could be a measure of stability of colloidal dispersions; in fact, this illustrates that the degree of repulsion between adjacent nanoparticles in dispersion. High zeta potential values for small molecules/particles indicate their proper electrical stabilities and high particles' aggregation avoidance. In case of low zeta potentials, attraction dominates the repulsion and one may face the aggregation and flocculation. It is observed that the value of approximately is $-43.5$ for zeta potential of the nanoporous graphene of 0.1 wt% in nanofluid. Is The group of intensity versus zeta potential is shown in Fig 5. Based on the previous descriptions, the nanofluid in this case is stable. The prepared nanofluids samples for different nanoporous graphene concentrations and times are shown in their containers in Fig. (6). It is found that the nanoporous graphene nanofluids remain relatively stable for 24 h.

![Figure 5](image)

**Figure 5.** The Zeta Potential of the Synthesized Nanoporous Graphene/DEA nanofluids

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>Nanoporous Graphene Concentrations (wt%) 0.005/0.01/0.05/0.1/0.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td></td>
</tr>
<tr>
<td>24</td>
<td></td>
</tr>
</tbody>
</table>

![Figure 6](image)

**Figure 6.** The Photos Representing the Prepared Nanoporous Graphene/DEA Nanofluids for 5 Different Nanosheet Concentrations at the Beginning and after 24 h of Preparing Nanofluids
### 3.2. Results of Experiments

To explain the process of absorption through nanofluid an Effective Absorption Ratio is applied. This parameter is defined as the mass of the gas absorbed by nanofluid divided by the mass absorbed by the base fluid and displayed by $R_{\text{eff}}$ (Esmaeili Faraj et al., 2014)

$$
R_{\text{eff}} = \frac{m_{A,\text{nf}}}{m_{A,bf}} = \frac{(C_{A,\text{out}} - C_{A,\text{in}})_{\text{nf}}}{(C_{A,\text{out}} - C_{A,\text{in}})_{\text{bf}}}
$$

where, $C_{A,\text{out}}$ and $C_{A,\text{in}}$ are the concentrations of $A$ (CO$_2$ or H$_2$S) in the gas phase at the outlet and the inlet of the test section, respectively. Likewise, “nf” and “bf” represent the nanofluid and the base fluid, respectively.

### 3.3. The Effect of Nanoporous Graphene Dosage on Falling Film Absorption

Here, the CO$_2$ and H$_2$S removal by nanofluids containing nanoporous graphene nanosheets in DEA (10 wt%) are measured. In these experiments the nanosheet dosage and the CO$_2$ and H$_2$S concentration in the feed gas stream are assessed.

In all tests the liquid flow rate is 0.7 cc/s. The $(N_{\text{Re}})$ of liquid falling film is determined to be below 50, which is in the laminar region (Danckwerks, 1970). The gas flow rate is set to the constant value of $9.33 \times 10^{-6}$ m$^3$/s. The temperature and total pressure of all experiments are kept at 298 K and 1.8 psig respectively and the total amine concentration is 10 wt.%.

The first experiment is performed by consuming DEA 10 wt.% as the absorbent in presence of CO$_2$ and H$_2$S in the feed gas. The effects of different operating parameters including H$_2$S and CO$_2$ concentrations in feed gas and concentration of nanoporous graphene are assessed. Different experiments including five various nanosheet concentrations are run while other conditions are kept constant. These concentrations are selected in order to determine the best concentration of the nanoporous graphene. Here, the nanosheet concentrations are 0.005, 0.01, 0.05, 0.1 and 0.5 wt %. The CO$_2$ effective absorption ratio versus nanoporous graphene concentration is obtained through these experiments for gas samples #1 and #2. The results are graphed in Fig. (7), where at all conditions, the $R_{\text{ef}}$ parameter is greater than unity.

When compared with consuming pure DEA, the maximum increase in theremoved CO$_2$ values observed are 39% at 0.1 wt.% of nanoporous graphene/DEA nanofluids and 34% at 0.1 wt.% of nanofluids, for gas samples # 1 and #2, respectively. As observed in Fig. 7, there is an increase in effective absorption ratio value due to the increase in particle concentration in the first section of the graph. However, a different trend happens in the second part of the graph and the effective absorption ratio begins to decrease in nanoporous graphene concentrations with a rate greater than 0.1 wt.%. The decreasing trend occurs when the nanosheets become too dense and $R_{\text{ef}}$parameters loose value. Based on the findings by Krishnamurthy et al (2006)and Lee et al. (2011) low disturbances in the velocity field of nanosheet at high concentrations, due to its aggregation and a decrease the diffusion mass transfer. Similar observations are reported by Krishnamurthy et al. (2006) and Fang et al. (2009) works.

![Figure 7. CO$_2$ Effective Absorption Ratio Versus Nanoporous Graphene Nanosheet Concentration for Graphene/DEA Nanofluid at 298 K](image-url)
The same procedure is applied for H$_2$S absorption. The values of effective absorption ratio of H$_2$S versus graphene nanosheet concentration are shown in Fig. 8 for both gas samples. As observed in Fig. (8), H$_2$S effective absorption ratio follows an increasing trend up to 0.1 wt.% nanoporous graphene, in both gas samples. Here, an improvement by 9% and 6% for samples #1 and #2 is observed at point 0.1 wt.% nanosheet fraction, i.e. the optimum and critical concentration of nanofluid), respectively. The graph trend changes after this point. The mechanisms of CO$_2$ and H$_2$S absorptions after the concentration of 0.1 wt.% become the same. As mentioned earlier when discussing Fig. 7, the decreasing trend in Fig. (8) is due to high aggregations in the nanosheets. Where, the R$_{eff}$ value becomes lower in the interval 0.1-0.5 wt% of nanosheets.

![Graph](image)

**Figure 8.** H$_2$S Effective Absorption ratio Versus nanoporous Graphene Nanosheet Concentration for Graphene/DEAnanofluid at 298 K

### 4. Conclusions

In this study, the effect of presence of nanoporous graphene nanosheet in DEA on simultaneous absorption of H$_2$S and CO$_2$ from a gas stream containing CO$_2$, H$_2$S and CH$_4$ is assessed in an experimental manner. The experiments are run at 298 K and at two different inlet gas concentrations. For this purpose, a wetted wall column at pressure of 1.8 psig is applied here. The nanofluids containing nanoporous graphene nanosheets are prepared by the GA surfactant through ultrasonic treatment which indicate acceptable stability. The results indicate that the nanoporous graphene-DEA nanofluid enhances H$_2$S mass transfer in relation to the base fluid up to 9% at 0.1 wt% nanosheet concentration. It is revealed that the CO$_2$ absorption rate is enhanced up to 39% at 0.1 wt% of nanoporous graphene/DEA nanofluids for sample # 1, and 34% at 0.1 wt% of nanoporous graphene/DEA for sample #2, respectively.

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