CAPTURA MELHORADA DE DIÓXIDO DE CARBONO POR NANOFLUIDOS CONTENDO NANOPARTICULAS INORGÂNICAS E LÍQUIDO ORGÂNICO DE LIGAÇÃO

IMPROVED CARBON DIOXIDE CAPTURE BY NANOFLUIDS CONTAINING INORGANIC NANOPARTICLES AND BINDING ORGANIC LIQUID

تحسين امتصاص ثاني أكسيد الكربون بواسطة السوائل النانوية التي تحتوي على جزيئات نانوية غير عضوية وسائل عضوي رابط

SHAKIR, Safa Waleed¹; WIHEEB, Ahmed Daham^{2*}; KHALAF, Zainab abdulmajeed³; OTHMAN, Mohd Roslee⁴

¹Tikrit University, College of Engineering, Chemical Engineering Department. Iraq.

²University of Diyala, College of Engineering, Chemical Engineering Department. Iraq.

³Samarra University, College of Archaeology, Iraq.

⁴Universiti Sains Malaysia, School of Chemical Engineering. Malaysia.

* Corresponding author

e-mail: ahmed_chem76@uodiyala.edu.iq

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RESUMO

A captura de dióxido de carbono (CO₂) tem sido a questão de pesquisa mais importante devido ao perigoso impacto das emissões de dióxido de carbono no aquecimento global e nas mudanças climáticas. Nas últimas décadas, uma nova tecnologia de absorção foi usada para se livrar do dióxido de carbono. Este procedimento está recebendo grande atenção sendo aplicado para melhorar a absorção de CO₂ usando nanofluidos. No entanto, outros estudos são necessários para melhorar a taxa de absorção / dessorção dos nanofluidos e diminuir as necessidades de energia através do processo de dessorção. Essa pesquisa objetivou estudar a influência da adição de nanopartículas por meio da determinação do fator de aumento da taxa de absorção / dessorção do dióxido de carbono. Todos os nanofluidos usados neste estudo foram preparados pela adição de nanopartículas com tratamento de ultrassom sem surfactantes. A influência da adição de nanopartículas à ligação de líquidos orgânicos (BOL) de mono etanolamina (MEA) e etanol na absorção / dessorção de CO₂ foi estudada experimentalmente em reator de agitação. Foram selecionadas as nanopartículas de Al₂O₃, Fe₂O₃ e SiO₂ que apresentaram diferentes propriedades para a investigação. Foram estudados o efeito da porcentagem de volume de nanopartículas, tipo de nanopartículas e velocidade de agitação na taxa de absorção de CO₂, bem como o efeito da porcentagem de volume de nanopartículas e tipo de nanopartículas na taxa de dessorção de CO₂. Foi descoberto que as nanopartículas suspensas em BOL são um absorvente promissor na infraestrutura MEA atual devido à sua natureza menos corrosiva e menores requisitos de energia para regeneração do que o MEA atual. Neste trabalho, a absorção de dióxido de carbono foi melhorada em 11% e a absorção de dióxido de carbono aumentou em 8,5% apenas com o BOL. O nanofluido de alumina a uma concentração de 0,05 absorveu o dióxido de carbono mais alto em 0,061 g/s. Por outro lado, o nanofluido de óxido de ferro a uma concentração de 0,01% em volume absorveu o dióxido de carbono mais alto de 0,0077 g/s.

Palavras-chave: Captura de CO₂, absorção, ligação de líquido orgânico, nanopartículas, fator de aumento de CO₂.

ABSTRACT

Carbon dioxide (CO₂) capture has been the most crucial research issue due to the dangerous impact of carbon dioxide emissions on global warming and climate change. In recent decades, a new absorption technology has been used to get rid of carbon dioxide. This procedure is getting tremendous attention being applied to improve CO₂ uptake by using nanofluids. However, other studies are needed to enhance the nanofluid absorption/desorption rate and decrease the requirements of energy through the desorption process. This research aimed to study the influence of addition nanoparticles by determining the enhancement factor of the absorption/desorption rate of carbon dioxide. All nanofluids used in this study prepared by adding nanoparticles

with ultrasound treatment without surfactants. The influence of adding nanoparticles to the binding organic liquids (BOL) of monoethanolamine (MEA) and ethanol on the absorption/desorption of CO₂ was studied experimentally in a stirring reactor. The nanoparticles of Al₂O₃, Fe₂O₃, and SiO₂ were selected, which showed different properties for the investigation. The effect of volume percentage of nanoparticles, type of nanoparticles, and stirring speed on the rate of CO₂ absorption and the impact of volume percentage of nanoparticles and type of nanoparticles on the CO₂ desorption rate were studied. It has been found that nanoparticles suspended in BOL are a good absorbent in the current MEA infrastructure due to their less corrosive nature and lower energy requirements for regeneration than the current MEA. In this work, carbon dioxide absorption was improved by 11% and carbon dioxide absorption increased by 8.5% from BOL alone. The alumina nanofluid at a concentration of 0.05 absorbed the highest carbon dioxide by 0.061 g/s. In contrast, the iron oxide nano particles at a concentration of 0.01 volume% absorbed the most elevated carbon dioxide of 0.0077 g/s.

Keywords: CO₂ capture, absorption, binding organic liquid, nanoparticles, enhancement factor.

المخلص

كان احتجاز ثاني أكسيد الكربون (CO₂) هو أهم قضية بحثية بسبب التأثير الخطير لانبعاثات ثاني أكسيد الكربون على الاحتباس الحراري وتغير المناخ. في العقود الأخيرة، تم استخدام تقنية امتصاص جديدة للتخلص من ثاني أكسيد الكربون. يُحظى هذا الإجراء باهتمام كبير يتم تطبيقه لتحسين امتصاص ثاني أكسيد الكربون باستخدام السوائل النانوية. ومع ذلك، هناك حاجة لدراسات أخرى لتحسين معدل امتصاص / امتصاص سائل النانو وتقليل متطلبات الطاقة من خلال عملية الامتصاص. الهدف الأساسي من هذا البحث هو دراسة تأثير إضافة جزيئات النانو من خلال تحديد عامل التعزيز لمعدل امتصاص / امتصاص ثاني أكسيد الكربون. تم تحضير جميع سائل النانو المستخدمة في هذه الدراسة عن طريق إضافة جزيئات النانو مع العلاج بالموجات فوق الصوتية بدون مواد خافضة للتوتر السطحي. تمت دراسة تأثير إضافة جزيئات النانو إلى السوائل العضوية الرابطة (BOL) للإيثانول الأحادي (MEA) والإيثانول على امتصاص / امتصاص ثاني أكسيد الكربون بشكل تجريبي في مفاعل التحريك. تم اختيار الجسيمات النانوية من Al₂O₃ و Fe₂O₃ و SiO₂ والتي أظهرت خصائص مختلفة للتحقيق. تمت دراسة تأثير النسبة المئوية للحجم من الجسيمات النانوية ونوع الجسيمات النانوية وسرعة التحريك على معدل امتصاص ثاني أكسيد الكربون وكذلك تأثير النسبة المئوية للحجم من الجسيمات النانوية ونوع الجسيمات النانوية على معدل امتصاص ثاني أكسيد الكربون. لقد وجد أن الجسيمات النانوية المعلقة في BOL هي مادة ماصة واحدة، نظرًا لطبيعتها الأقل تآكلًا وانخفاض متطلبات الطاقة اللازمة للتجديد مقارنة بالـ MEA. في هذا العمل، تم تحسين امتصاص ثاني أكسيد الكربون بنسبة 11% وزيادة امتصاص ثاني أكسيد الكربون بنسبة 8.5% من BOL وحده. امتص سائل الألومينا النانوي بتركيز 0.05 أعلى ثاني أكسيد الكربون بمقدار 0.061 جم / ثانية، بينما امتص أكسيد الحديد النانوي بتركيز 0.01 حجم% أعلى ثاني أكسيد كربون قدره 0.0077 جم / ثانية.

الكلمات المفتاحية: التقاط ثاني أكسيد الكربون، الامتصاص، السائل العضوي الملزم، الجسيمات النانوية، عامل التحسين.

1. INTRODUCTION:

Nowadays, air pollution is considered the biggest curses facing the planet due to its impact on climate change and public and individual health that causes an increase in disease and death. Several pollutants are among the main factors that cause disease in humans (Manisalidis *et al.*, 2020). These pollutants include particulate, which are particles of very small in diameter that enter the inhalation system through breathing, causing diseases in respiratory and vascular, cancer, and dysfunction in the generative and nervous system. Also, sulfur dioxide, nitrogen oxide, dioxins, volatile organic compounds, and polycyclic aromatic hydrocarbons are considered harmful air pollutants.

Furthermore, Carbon monoxide can also cause direct poisoning when inhaled at high levels. The geographical distribution of many infectious diseases is affected by climate change caused by environmental pollution and natural disasters. The public consciousness, combined with an interdisciplinary team of scientific specialists, considers the only way to remedy this problem (Manisalidis *et al.*, 2020).

Without the slightest doubt, all declared above

is so associated with climate change, and if the danger does occur, the consequences can be dire for humanity (Radu *et al.*, 2016). The warming of the globe and the climate change affects the planet seriously affect many ecosystems, causing problems with food safety issues, melting ice and glaciers, animal extinction, and damage to plants (Munang, 2013).

The increase of greenhouse gases (GHGs) in the atmosphere raises the average global temperature and causes climate change. The growth of these gases lets the short sunlight wave's energy move into the atmosphere reaching the ground without being limited. When the wave energy reaches the earth's surface, some of the longer wave energy is emitted as heat to the atmosphere again. The heat traps in the atmosphere (lower layer) by GHGs (Carpenter *et al.*, 2013). The GHGs in the atmosphere involves 81% of carbon dioxide (CO₂), 6% nitrous oxide (N₂O), 11% methane (CH₄), and 3% fluorinate gases. The atmospheric composition is severely influenced by the growth of the GHGs, causing a reduction of the stratospheric ozone layer. During the 20th century, the first CO₂ analyzer had been finished, and this indicated that the CO₂ concentration in the atmosphere had improved significantly. Since the commencement of the

industrial's age, the CO₂ anthropogenic emissions have increased dramatically as a result of the burning of vast quantities of fossil fuels, such as coal, natural gas, petroleum, and diesel, used to generate electricity and transportation (Mondal *et al.*, 2012)

However, CO₂ emission has been the main subject in research concerning global issues. The normal concentration of CO₂ in the air has been hastily growing and, at present, is about 418 ppm (Scripps Institution of Oceanography 2020). This growth made a terrible problem for humans and many species of animals, for a sum of reasons. The most exposed concern is climate change. The association of increased CO₂ to global warming was well understood that the increase of atmospheric energy would raise the atmospheric temperatures and weather. However, climate change may not be a big concern for many people because it does not appear disastrous.

In this century, it may be possible to overlook the effects of the 5°C temperature increase by relocating to a more relaxed and safer geographical location. Alternatively, it is conceivable that humans have ignored the direct and instantaneous deadly feature of CO₂ increasing in the atmosphere. The CO₂ concentration levels in the third atmosphere of the Earth have already been outside the range of humans breathes during their evolution. As all know, when carbon dioxide levels are high, inhalation of carbon dioxide becomes toxic to humans, with many deaths reported based on working exposure. Based on comparatively instant clarifications of fitting and healthy, the limit of CO₂ exposure was set as 5000 ppm (part per million) for an eight hours exposure in the workday (Zhang *et al.*, 2017). So, the harmless limit of CO₂ concentration for lifetime exposure will be considerably lower than this limit. Moreover, with the increase in human CO₂ emissions, several researchers expect that there will be toxic effects shortly (McNeill and SAS 2016; Augusto *et al.*, 2018).

For all the above, reducing carbon dioxide from its emissions is a global concern that needs a robust and swift solution to slow the growing risk affecting climate change and global warming (Mondal *et al.* 2012). The industry accounts for almost 40% of worldwide CO₂ emissions, an essential point of concern (Marlon *et al.*, 2019). Several plans have been accounted for to decrease emissions of CO₂: post-combustion, pre-combustion, oxy-fuel combustion, and electrochemical separation. Capturing CO₂ from post-combustion is the most direct strategy for

application in existing processes. However, it is the most challenging application because of the deficient CO₂ concentration and pressure (about 12–15 mol. %) of the flue gas, and the low rate of the carbon recovered compounds (Fujimoto *et al.*, 2016; Wiheeb *et al.*, 2018).

Nonetheless, the increase of carbon dioxide produced from flue gas pretenses a real danger of global warming. Therefore, the removal of carbon dioxide is critical and has received increasing interest from energy researchers worldwide. Several approaches can be useful to reduce carbon dioxide production, such as using renewable fuels instead of fossil fuels and trying to seize carbon dioxide from its large emissions (Rocha *et al.*, 2016). The separation is a promising technique to control the CO₂ emissions from its source (Mondal *et al.*, 2012; Wiheeb *et al.*, 2018). Many technologies are used to remove CO₂ such: absorption, adsorption and gas-separation membranes. 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 (Araújo and de Medeiros, 2017). The chemical or physical absorption process is the standard method used to remove CO₂. The absorption process is one of the best established and mature procedures for CO₂ removal from large emission sources is through chemical absorption utilizing alkanolamine solvents. This technology has been proven to work successfully to separate CO₂ for decades (Yuan and Rochelle, 2019).

However, the treatment cost of fixed emission sources using this method is high due to increased energy consumption. The leading energy expended in alkanolamine solvents is about 80% of the total cost consumed through solvent regeneration. In contrast, the rest of the energy required comes from the pumps, refrigeration system, and compressor. In this technique, the solvent selection is an essential factor in designing the absorption process because this will improve equipment size while reducing operating costs. The choice of the absorbent depends on its turnover rate, and the heat of regeneration and corrosion problems can have an essential influence on the reactant absorption process as a result of its impact on the total costs (Wiheeb *et al.*, 2018; Conway *et al.*, 2014). Alkanolamines are the most used solvents to capture the acid gas commercially. These solvents include Monoethanolamine (MEA), Diethanolamine (DEA), and Triethanolamine (TEA) (Olajire, 2010; Meldon *et al.*, 2011; Budiman *et al.*, 2015; Hemmati *et al.*, 2019; Yuan and

Rochelle 2019). MEA has been the most common solvent used industrially because of its high ability to absorb CO₂, simplicity in use, low cost, and availability. However, the MEA performance is limited by numerous factors, including the high energy requirements for the regeneration, oxidative degradation, and corrosion concerns (Yuan and Rochelle 2019). Research for alternative solvents with improved absorption/desorption of CO₂ is thus needed to cope with the MEA unsustainability.

A new class of binding organic liquid (BOL) has been presented as solvents for CO₂ capture (Mathias *et al.*, 2015). The use of binding organic liquids for CO₂ capture (CO₂-BOLs) had been recommended in the previous work involved organic bases with alcohol (Zhang *et al.*, 2013). This kind of solvent uses alcohol instead of water to decrease energy consumption used for regeneration and solve the corrosion problems. Results from their experiment revealed that CO₂-BOLs solvent was superior to alkanolamine in terms of the former's higher CO₂ loading capacities, less corrosiveness, successful absorption of other acid gases such as SO₂, COS, with decreasing the regeneration energy requirement (Liu *et al.*, 2017; Dejan *et al.* 2018).

The chemical and physical absorption of CO₂ occurred when the CO₂ gas transfer from the gas phase to the liquid phase due to the difference in concentration. This transport phenomenon can be described well by the theory of the two films, as shown in Figure 1. The solute diffused from the bulk of the gas phase, through the gas-film and across the interface. The solute in the liquid film can be reacting chemically with solvent (Wang *et al.*, 2018).

The reaction mechanism was planned according to the interaction of amines with CO₂. The researches attempted to apply the theory of amine interaction with CO₂ to become relevant for the novel solvent system. There are several studies show that the final product of the CO₂ reaction with the alcohol solution is alkylcarbonate salts similar to bicarbonate and carbamate salts when the aqueous solutions of the amine interact with CO₂ (Barzagli *et al.*, 2013).

Recent studies applied the nanotechnology in the absorption process to enhance the performance of solvent. The nanoscale solid's dispersion in the solvent to enhance both mass and heat transfer has been a new attractive research field that has recently applied in some research. It has been found that the very high thermal conductivity of the nanoparticles plus the

nanoscale convection induced by the Brownian motion leads to enhance heat transfer (Kim *et al.*, 2012). According to the similarities between mass and heat transfer phenomena, it was expected that nanofluids would have the same effect on enhancing mass transfer. It has been shown that nanofluids increase the mass transfer also compared to the primary fluids before adding the nanomaterials (Kim *et al.*, 2012; Ashrafmansouri *et al.*, 2014). Therefore great attention has been given to nanofluids to enhance heat and mass transfer as next-generation working fluids.

In another development, it was discovered that the use of nanofluid containing nanoparticles and solvent (Bahmanyar *et al.*, 2011) could increase the CO₂ absorption rate (Ashrafmansouri *et al.*, 2014) more effectively than the solvent alone (Keshishian *et al.*, 2013). Nanofluid was formed by adding nanoparticles of 80 nm in diameter into a water-free solvent such as alcohol, and the particles were maintained in suspension in the fluid. The nanofluids' research is gaining momentum recently due to its less corrosiveness and lower temperature requirement for regeneration than its MEA counterpart. Nanofluids are a promising candidate to replace the MEA in the future.

In addition to its favorable characteristics in CO₂ capture, nanofluids can also use the existing MEA infrastructure, eliminating the need for an expensive capital upfront if nanofluid was used to replace MEA. However, before nanofluid can make its way into the industry to replace MEA, there are fundamental issues that need to be resolved first. The most vital issues revolve around the nano-particles interaction and the gas-liquid mass transfer that need explanation (Zhang *et al.*, 2013; Mathias *et al.*, 2015). Additional research to explain the effect of micro-scale interaction and types of nanoparticles and sizes on the CO₂ absorption is also imperative. This research aimed to study the effect of different types of nanoparticles, namely SiO₂, Fe₂O₃, and Al₂O₃, on the CO₂ absorption/desorption by water-free nanofluids.

The CO₂ absorption and desorption rate of the solvent is determined by the difference in CO₂ gas rate between the inlet and outlet of the absorber from the gas phase by using a CO₂ gas analyzer (Liu *et al.*, 2017) as in the following equations.

$$r = \frac{Q_{in} - Q_{out}}{m * 22.4 * 1000} \quad (\text{Eq. 1})$$

Where r : the solvent absorption rate (mol /kg. min). Q_{in} : Inlet gas flow rate (ml/min). Q_{out} : Outlet gas flow rate (ml/min). m : Quality of the solvent (kg).

Then, the influence of nanoparticles' presence on the CO_2 absorption rate, E_a , was quantified by a CO_2 absorption enhancement factor, which is defined in (Eq. 2) (Jiang, *et al.*, 2014).

$$E_a = \frac{\text{CO}_2 \text{ absorption rate in the presence of nanoparticles}}{\text{CO}_2 \text{ absorption rate in the absence of nanoparticles}} \quad (\text{Eq. 2})$$

The effect of nanofluids on the CO_2 desorption rate, E_d , was determined by CO_2 desorption enhancement factor, which is defined in (Eq. 3):

$$E_d = \frac{\text{CO}_2 \text{ desorption rate in the presence of nanoparticles}}{\text{CO}_2 \text{ desorption rate in the absence of nanoparticles}} \quad (\text{Eq. 3})$$

2. MATERIALS AND METHODS:

2.1. Preparation of nanofluids

The nanofluids used in the absorption experiments were prepared following a two-step method. The first step was the preparation of BOL solvent by mixing 1:1 molar ratio of MEA (C_2H_7NO , 98%, Merck) with ethanol (C_2H_5OH , 99.8%, sigma-Aldrich) and then stirring for 15 minutes at room temperature to obtain a homogeneous solution. The second step was the addition of nanoparticles with 80 nm in diameter of SiO_2 , Fe_2O_3 and Al_2O_3 (with a purity of 99% acquired from 99%, sigma-Aldrich) to the homogeneous BOL solvent at different concentration (0.5-0.15) vol.%. After each addition, the nanoparticles dispersed in the solution by ultrasonic wave to ensure uniform dispersion throughout the solution medium (BOL solvent). The prepared BOLs nanofluids with high nanoparticles vol. % containing SiO_2 , Al_2O_3 , and Fe_2O_3 nanoparticles had been visualized for 24 hours, as shown in Figure 2.

2.2. Experimental procedure of CO_2 absorption

The absorption of CO_2 was performed at a room temperature of 298 K and atmospheric pressure. A glass cell reactor of 100 mL containing the BOL nanofluid stirred and fixed on certain

stirring speed (1-4) rotation per second (rpm). CO_2 (99.99%, SDI Samarra, Iraq) and N_2 (99.99%, acquired from SDI Samarra, Iraq) were used as received and supplied at the preferred volume percentage of 15 vol. % CO_2 and 85 vol. % N_2 using calibrated flow meters gas and mixed to produce 200 L/h gas mixture replaced and flowed into the nanofluid cell reactor to make direct contact with the solvent. The gas bubbled out from the solution was analyzed with a CO_2 analyzer every one minute until the solvent reaches the saturation limit (no more CO_2 was absorbed). Then, the absorption rate was determined by (Eq.1). The schematic of the experimental setup for the CO_2 absorption process is presented in Figure 3.

Figure 3. Schematic diagram of the CO_2 absorption process.

2.3. Experimental procedure of CO_2 desorption

The desorption rate of CO_2 , the solvent, and nanofluids were performed following the previous work (Nwaoha *et al.*, 2016; Wiheeb *et al.*, 2018; Yuan *et al.*, 2019). The experimental device consisted of a heating plate that provides the desorption energy requirement to the insulated oil bath. The 40 mL of the saturation solvent was placed into a 100 mL desorption reactor and immersed into an oil bath to reduce the heat losses which is fixed at the needed desorption temperature. The desorption reactor dipped in the oil bath until the desorption reactor's neck to lessen the heat losses. During the process, cold water runs into the condenser to decrease solvent loss due to evaporation. More than one thermometer was located to monitor the required temperature of 393 K. The first thermometer was located in the desorption reactor.

In contrast, the second was located in an oil bath. Also, The sample of the solvent saturated with CO₂ was agitated for 60 minutes at 393 K. The outlet gas from the top of the condenser was analyzed with a CO₂ analyzer until no more CO₂ was liberated. Then, the desorption rate was determined by (Eq.1). Figure 4 shows the schematic diagram of the desorption process setup.

Figure 4. Schematic diagram of the CO₂ desorption

Also, for more checking the weight difference before and after the absorption/desorption process after reach the max. The limit of CO₂ absorbed/desorbed was measured using an analytical balance with a readability of 0.0001g following the previous method (Kim *et al.*, 2017).

Then, nanofluids' effect on the CO₂ absorption rate was determined by CO₂ absorption enhancement factor E_a , which is defined in (Eq. 2).

Also, the effect of nanofluids on the CO₂ desorption rate, E_d , was determined by the CO₂ desorption enhancement factor, which is defined in (Eq. 3)

3. RESULTS AND DISCUSSION

3.1 CO₂ absorption rate of nanofluids

The effect of adding SiO₂, Fe₂O₃, and Al₂O₃ nanoparticles at the predetermined volume percent of 0.005, 0.01, 0.05, 0.1, and 0.15vol.% to the BOL solvent on the CO₂ absorption rate at room temperature is presented in Figure 5.

The CO₂ absorption rate for BOL solvent without adding any nanoparticle was 0.0055 g/s, such as shown by the dotted horizontal line. The added nanoparticles provided marked

improvement of the CO₂ absorption rate. The highest CO₂ absorption rate of 0.0061 g/s was obtained when 0.05 vol.% of alumina nanoparticle was added in the BOL solvent. Fe₂O₃ and SiO₂ nanoparticles at the same level of the nanoparticle concentration in the solution improved the CO₂ absorption to some extent but were generally inferior to Al₂O₃ nanoparticles. The nanofluids' increased absorption could be explained by the affinitive effect of the dispersed nanoparticles for the CO₂ gas in the BOL medium. The nanoparticles behaved like a magnet that attracted more CO₂ onto the solid's micropores and successfully held the gas molecules on their micropores for some time until the gas molecules were desorbed. The affinitive characters of silica (Othman *et al.*, 2009) and alumina (Helwani *et al.*, 2012) for CO₂ gas molecules were also reported in the previous work.

Figure 6 shows the effect SiO₂, Fe₂O₃, and Al₂O₃ nanoparticles on the CO₂ absorption enhancement factor. An enhancement factor of greater than 1 suggests favorability of CO₂ absorption by the nanoparticles over the BOL solvent. The CO₂ absorption by alumina nanoparticles at 0.05 vol.% concentration in the nanofluid was enhanced by a factor of 1.09, which constituted the experiment's maximum enhancement factor. Although silica nanoparticles could achieve the same factor as that of alumina nanoparticles, the former nanofluid was not an acceptable choice since it required a lot more volume (0.1 vol. %) of silica nanoparticles to effect the same affinity as that of 0.05 vol.% alumina nanoparticles. In this respect, silica nanofluid would be a more costly alternative. The result also implies that alumina nanoparticles exhibited the highest affinitive character for CO₂ molecules, followed by silica and iron oxide nanoparticles.

In addition to the nanoparticles' affinitive characteristic, the enhanced CO₂ absorption of alumina nanofluid can also be explained by the Brownian motion of the convective flowing gas molecules that heightened the gas-liquid mass transfer as described previously (Jiang *et al.*, 2013). However, the addition of more than 0.05 vol.% nanoparticles caused the Brownian flow to cripple due to the narrower and more constricted space (high viscosity) when more nanoparticles were present in the fluid medium (Kim *et al.*, 2008). The other mechanisms for the enhanced absorption performance are summarized in Figure 7. The first mechanism is the bubble breaking by the suspended nanoparticles that actively split the interface between the gas bubbles and liquid to form smaller bubbles for more effective absorption

by the nanofluid (Veilleux, and Coulombe, 2011). The second mechanism is associated with the hydrodynamic effect upon collision of the nanoparticles at the gas-liquid interface that led to local turbulence. The turbulence caused a new boundary layer between the gas and liquid to develop, eventually inducing the gas molecules to blend into the bulk liquid (Pashaei *et al.*, 2018). The third mechanism is the shuttle effect because of an additional quantity of gas adsorbed by the nanoparticles in the gas-liquid diffusion layer, and then the adsorbed gas was desorbed into the bulk liquid.

Figure 8 shows the speed effect of stirring on the enhancement factor of CO₂ absorption using different nanofluids. The concentration of the nanoparticles in the fluid medium was maintained at 0.05 vol.%. An increase of stirring speed would increase the broken gas bubbles' contact area with the bulk liquid and nanoparticles and the growth in the Brownian motion, increasing CO₂ absorption. The CO₂ absorption improvement factor increased with the increasing stirring speed for all the three types of nanoparticles. However, the enhancement factor did not improve for Al₂O₃ nanofluid despite increasing the stirring speed from 3 to 4 rps, possibly due to the shuttle effect's reduction. The alumina nanoparticles could not hold the adsorbed CO₂ under turbulence caused by the stirring for long. The gas was immediately desorbed into the bulk liquid as soon as the nanoparticles adsorbed the gas. Hence, the incremental rise in CO₂ absorption at the increasing stirring speed was not observed.

3.2 CO₂ desorption rate from the CO₂ rich nanofluids

Figure 9 shows the CO₂ desorption rate from the rich nanofluids. CO₂ desorption rate for BOL solvent without nanoparticles was 0.0071 g/s (indicated by the dotted line). The CO₂ desorption rate was generally low in this work due to the difficulty of maintaining the CO₂ in the liquid at the ambient temperature. The application of heat during the process of desorption exacerbated the condition. Heat is known to provide the energy to CO₂ to liberate itself from the absorbate and absorbent. The application of heat to desorb CO₂ effectively in a pressure swing adsorption (PSA) was reviewed quite extensively in the past (Wiheeb *et al.*, 2016).

It was observed that the desorption rate of CO₂ increased with the increase of the nanoparticles' concentration up to a certain level and then decreased. The highest CO₂ desorption was observed for iron oxide nanofluid at 0.0077 g/s, followed by Al₂O₃ and SiO₂ nanofluids. The

different trends on the CO₂ desorption capacity by the three nanofluids could be due to the different thickness of the diffusion boundary layer (Ma *et al.*, 2009; Yang *et al.*, 2011) and the bulk viscosity of the fluid medium (Jung *et al.*, 2012). The different trends might also be induced by the different specific heat of the nanoparticles in the fluid. The trend seemed to follow the particular heat of the nanoparticles in the order of iron oxide (104 J.kg⁻¹.K⁻¹), alumina (451 J.kg⁻¹.K⁻¹), and silica (703 J.kg⁻¹.K⁻¹) that promoted the self-diffusion in the nanofluids (Turanov *et al.*, 2009).

Self-diffusion increased when there was an increase in the contact between the gas and liquid (Kwark *et al.*, 2010). Generally, the stability of the nanoparticles declined with the increasing amount of the absorbed CO₂. Figure 10 shows the effect of nanoparticle addition on the CO₂ desorption enhancement factor. The highest CO₂ desorption enhancement factor of 1.09 was observed for the low concentration of iron oxide nanofluid at 0.01 vol.% (which is precisely similar to the CO₂ absorption enhancement factor of 1.09 by alumina nanofluid at a concentration of 0.05 vol.%), followed by 0.05 vol.% Al₂O₃ with a desorption enhancement factor of 1.07 and 0.05 vol.% SiO₂ nanofluids with a desorption enhancement factor of 1.04. The addition of nanoparticles in BOL solvent improved the CO₂ desorption enhancement factor significantly due to the heat transfer mechanism discussed earlier in the previous reports (Kebinski *et al.*, 2002; Fan, and Wang, 2011; Pang *et al.*, 2012).

Figure 11 summarizes the CO₂ desorption mechanisms from nanofluids. The first mechanism described the CO₂ desorption process as a boiling process. The fluid phase changed as the fluid temperature increased, and CO₂ started to bubble out (desorb from the liquid) due to solubility differences. When there was nanoparticle in the fluid, nanoparticles' presence affects the heat transfer by way of gravity and natural convection. The suspended nanoparticles improved the heat transfer by continuously falling-down and moving-up in the fluid medium as the nanoparticles released and received the heat energy (a second mechanism) from the heater surface. The thermal conductivity of the nanoparticles could ascribe the third CO₂ desorption mechanism. The thermal conductivity of alumina, iron oxide and silica nanoparticles are 30 W.m⁻¹.K⁻¹, 2.2 W.m⁻¹.K⁻¹, and 1.38 W.m⁻¹.K⁻¹, respectively. The order of CO₂ desorption enhancement factor was observed to strictly follow the order of the nanoparticles' thermal conductivity if the concentration of the nanoparticles was to be maintained at 0.05 vol.%.

For example, at 0.05 vol.% concentration, the enhancement factor for alumina, iron oxide, and silica nanofluids was 1.07, 1.05, and 1.04 (refer to Figure 10). To recapitulate, the higher the thermal conductivity, the better the heat energy was dissipated to the entire nanofluid medium and transferred to CO₂ molecule for the gas molecule to liberate itself (desorb) from the fluid.

4. CONCLUSIONS:

There was an 11% increase in CO₂ absorption and an 8.5% increase in CO₂ desorption when nanofluids were used. Al₂O₃ nanofluid at 0.05 vol.% concentration was capable of absorbing CO₂ the highest (0.061 g/s) followed by silica nanofluid at 0.1 vol.% concentration (0.060 g/s) and iron oxide nanofluid at 0.05 vol.% concentration (0.059 g/s). Whereas, iron oxide nanofluid at 0.01 vol.% concentration desorbed CO₂ the highest (0.0077 g/s), followed by alumina nanofluid at 0.05 vol.% (0.0075 g/s) and silica nanofluid at 0.05 vol.% (0.0072 g/s). The nanofluids' three absorption mechanisms were identified, namely the bubble breaking, the hydrodynamic effect, and the shuttle effect. Three mechanisms of desorption by the nanofluids were known to prevail in the experiment. They were solubility difference, nanoparticles energy, and their thermal conductivity. From the perspective of CO₂ absorption and desorption enhancement factor, alumina nanofluid appeared to be a promising candidate for alternative solvent in the existing MEA infra-structure due to its high reversibility absorption-desorption effectiveness in acid gas removal without the corrosive and high energy requirement issues.

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Figure 1. The absorption transport phenomena

(a)

Figure 2. Nanofluids containing (a) Al_2O_3 (b) Fe_2O_3 and (c) SiO_2 nanoparticles

Figure 5. CO₂ absorption by nanofluids at different vol.% of the nanoparticles

Figure 6. An enhancement factor of CO₂ absorption rate in the BOL with different types of nanoparticles and different vol. %.

(a)

(b)

(c)

Figure 7. Schematic diagram of nanofluid mechanisms: (a) bubble breaking, (b) hydrodynamic, and (c) shuttle effects

Figure 8. The influence of stirring speed on the enhancement factor of CO₂ absorption rate in the BOL solvent with different nanoparticles at 0.05 vol. %.

Figure 9. Desorption rate of the BOL and nanofluids.

Figure 10. An enhancement factor of the CO₂ desorption by the nanofluids

(a)

(b)

Figure 11. Schematic diagram of nanofluid desorption mechanisms: (a) solubility difference, (b) nanoparticles energy, (c) thermal conductivity