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Removal of Carbon Dioxide Using Water-in-Oil Emulsion Liquid Membrane Containing Triethanolamine

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Abstract: Liquid membranes are emerging as solid, liquid and gaseous extractors, replacing the conventional methods of separation for metals, enzymes and gases. For carbon dioxide separation, amine based chemical absorption have been commercially used because of their ability to form complexes at moderate temperature. However, the use of chemical absorption using aqueous amine can caused corrosion. Emulsion liquid membrane becomes an alternative to reduce the contact between the amines and metal surfaces. This paper discusses the preparation of emulsion liquid membrane using triethanolamine (TEA) as an extractant to remove carbon dioxide. The emulsions were prepared by varying the concentration of the extractant and the surfactant, in order to obtain a stable emulsion that can effectively remove carbon dioxide from gas mixtures. High speed homogenizer was used to produce micro-sized emulsion that can increase the mass transfer of carbon dioxide from the gas phase to the liquid phase. It was found that the optimum amount of surfactant (Span 80) in the organic phase and extractant (TEA) in the aqueous phase to produce stable emulsion is 6 vol %. A stable micro-sized emulsion was produced at a stirring speed of 20,000 rpm for 3 hours. This emulsion liquid membrane can remove 88 % of the carbon dioxide introduced into the rotating disc contactor.

Key words: Removal, carbon dioxide, triethanolamine, emulsion liquid membrane.

INTRODUCTION

There is a need for carbon dioxide separation in many industrial applications such as in natural gas processing, landfill recovery, enhanced oil recovery and upgrading the gas generated from biological wastes. Carbon dioxide removal attracts more attention than other impurities due to its corrosive behavior. Removing carbon dioxide to a level of less than 1 % is essential to avoid corrosion of pipeline and equipment as well as to meet fuel gas specifications for natural gas since carbon dioxide reduces the heating value of the gas[1]. At present, the capture and separation of carbon dioxide can be achieved by different approaches, namely chemical and physical absorption using solvents, solid physical adsorption, cryogenic techniques, and membrane separation[2, 3]. The most established method is by absorption into amine solution via packed towers, spray towers, or bubble columns. However, the liquid amine based processes pose operating difficulties in keeping the operation clean and to operate within the process constraints[4]. Besides, this process also suffers from high regeneration energy requirement, large equipment size, corrosion and solvent leakage that require more efficient and flexible methods[5].

Nowadays, emulsion liquid membrane offers a great potential to many industrial, environmental and biomedical systems[6 – 10]. The emulsions are colloidal systems that made of liquid droplets dispersed in another liquid phase. They are produced by shearing the two immicible liquids, which provides the necessary energy to reach metastable state through fragmentation of one phase into another[7]. Since the droplet formed tends to coalesce, surfactant is added to stabilize the newly formed droplets. Water-in-oil-in-water (w/o/w) consists of small water droplets contained within larger oil droplets, which are dispersed in water continuous phase. They are usually created using conventional homogenization technology in several steps procedure[11]. Direct emulsions consist of oil droplet dispersed in aqueous continuous phase is also known as oil-in-water (o/w) emulsion whereas inverse emulsion are made of water-in-oil (w/o). In o/w type emulsion, the mass transfer coefficient is not affected by the content of the oil phase, whereas in the w/o type of emulsion, the coefficient increases proportional to the volume fraction of oil. In the

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separation process using emulsion liquid membrane, the dispersed drop sizes as well as internal droplets are important in determining the efficiency of extraction or separation, the stability of the emulsion, and the interfacial contact area. The stability is dependent on the internal droplet interactions that are also related to several factors such as electrostatic repulsive forces and hydrodynamic forces[12].

The absorption of carbon dioxide into the emulsion liquid membrane that contains amine may become the alternative method for carbon dioxide removal. Since the amine formed as droplets and dispersed in the organic phase, it does not directly get into the contact with metal surfaces. Hence, the corrosion problem can be avoided. In addition, the formation of micro-size droplets increases the surface area, thus increase the transfer rate of carbon dioxide. Therefore, among factors that need to be considered for the separation of carbon dioxide using emulsion liquid membrane are the effect of surfactant and the extractant on the stability of the emulsion. This is due to the fact that the emulsion is generally unstable. However, several experimental evidences have shown that some emulsion formulation are stable up to several hours and days using different types of surfactant. The emulsion is considered stable if it persists at least five days at 15ºC[13]. The persistence of such dispersion of emulsion is generally ensured by the presence of surface active species (surfactant or polymer molecules) which are known to cover the interfaces and delay the recombination or coalescence of the droplets[7].

In the w/o emulsion, an aqueous phase is being stabilized by oil soluble surfactants. The surfactant strongly absorb to the oil-water interface, which lowers the interfacial tension and/or provides kinetic barrier that prevents droplet coalescence[14]. The aqueous phase can finely disperse in the organic phase and functions as a selective barrier, or membrane. In the gas separation process, the gas passed through the system and transferred across the membrane into the aqueous phase (NaOH/TEA solution). The mass transfer is driven by the concentration difference between the external feed phase and the internal aqueous phase. The concentration of the solute in internal phase is typically kept at zero concentration in order to maintain the concentration gradient, until most of the substance is extracted from the external phase. Since amines (such as monoethanolamine, diethanolamine, triethanolamine) have high selectivity towards carbon dioxide, it can be used to facilitate the removal of carbon dioxide in the emulsion liquid membrane system. Thus, a good formulation of emulsion liquid membrane is very crucial to ensure that the process is capable of removing carbon dioxide from any gas mixtures. This paper presents the stability study of w/o emulsion liquid membrane using triethanolamine (TEA) as an extractant and the removal of corbon dioxide using the emulsion liquid membrane in a rotating disc contactor.

MATERIALS AND METHODS

Water-in-oil (w/o) emulsion liquid membrane consists of organic and aqueous phases. In this study, the organic phase consists of kerosene (organic solvent) and Span 80 (surfactant), whereas the aqueous internal phase comprised of NaOH solution and triethanolamine (TEA). The organic phase was prepared by dissolving Span 80 in the kerosene at different concentrations. The method was repeated for different amount of surfactant (2 vol %, 4 vol %, and 6 vol %). The aqueous phase was prepared by adding and stirring the extractant (TEA) into the NaOH solution until it form a homogeneous solution. The amount of TEA was also varied (2 vol %, 4 vol %, and 6 vol %) to observe the effect of extractant on the stability of the emulsion.

High performance disperser (Ultra Turrax® T25) with 18G mixing shaft was used for the preparation of the emulsion. Initially, the organic phase that consists of kerosene and Span 80 was homogenized at 10,000 rpm while the internal aqueous stripping phase was poured drop wise. The solution was prepared using three different speeds; 10,000 rpm, 15,000 rpm and 20,000 rpm. Since emulsification time may also affect the droplet size and stability of the emulsion, the time interval of 60 minutes, 120 and 180 minutes were used for each formulation. The stability of the emulsion was determined at room temperature (25 ± 2ºC). After 24 hrs, the emulsion stability was determined based on the separation of the aqueous and organic phase.

Figure 1 shows the experimental apparatus in which the emulsion liquid membrane was used to absorb carbon dioxide by aqueous amine solution. In the operation, the amount of carbon dioxide absorbed in the emulsion liquid membrane was determined using the most stable emulsion liquid membrane prepared. The gas stream flowed into the rotating disc contactor (RDC) via gas distributor at the bottom of the column. The pressure of the gas maintained at 25 psi. The rotating disc contactor (RDC) is used to stabilize the emulsion in the contactor column and to increase the mass transfer rate of the solute (carbon dioxide) by increasing the contact between the gas and the emulsion. The absorption was carried out for 30 minutes to reach steady state condition. The outlet gas stream is connected to gas chromatography unit (Agilent 3000A) to measure carbon dioxide concentration.

RESULTS AND DISCUSSIONS

In the emulsion liquid membrane system, the formation and breaking of oil-water emulsion is extremely important. Despite of the fascinating features of ELMs, this technology is not widespread because of the two main hindrances: (1) instability of the liquid membrane and (2) the swelling of emulsion. It has been stated that the emulsion stability is the 'Achilles heel' of the ELM process[15] and the unsolved difficulties with emulsion stability have once diminished the direction of enlarging the process scale[16]. However, several researches have shown that the stability of emulsion can be achieved by adding additives. In general, the stability of the emulsion is generally defined as the resistant of the liquid membrane to leakage (or rupture) under high shear stress during the operation of solute extraction in ELM process. In contrast, unstable liquid membrane is subject to be broken apart and release the internal stripping phase and the extracted solutes to the external feed phase, which nullify some of the solute separation already achieved[17].

As proposed by Gray[2], the majority of the carbon dioxide captured by amines result in the formation of bicarbonate in the liquid amine capture system. The mechanism of reaction between carbon dioxide and amines is shown in Fig. 1. In the aqueous media, there is a requirement of 2 mol-amine/mol carbon dioxide for the formation of bicarbonate compounds during the capture of carbon dioxide.

In order to increase the gas separation in the emulsion liquid membrane system, it is important to have large surface area. This can be achieved by having small and uniform droplets. In addition, uniform droplets will also produce a stable emulsion. This study reveals the effect of surfactant (Span 80) and extractant (TEA) on the droplet size. The surfactant, Span 80, increases and optimizes the preferential interfacial curvature, thus the interfacial tension reduced. Therefore, as the concentration of Span 80 increases, the size of particle decreases[18]. As shown in Figure 3(a), the emulsion containing 2 % (v/v) surfactant concentration is less stable. Those unstable particles coalesce rapidly among themselves resulting bigger particle. As the amount of Span 80 increases, a more stable and smaller particles are formed. In this study, surfactant (Span 80) has been used to delay the separation of the organic and aqueous phase. This additive strongly adsorbs to the oil-water interface and lowers the interfacial tension (the main driving force for demixing). As the surfactant lowers the interfacial tension, the size of the droplets also decreases, which consequently enhances the emulsion stability. The resistance of an emulsion droplet to deform is governed by the magnitude of its Laplace pressure, which is controlled by the interfacial tension of the surfactant[9,19]. The stability increases as the concentration of Span 80 increases. At 6 vol %, the emulsion is 97 % stabilized. However, it is important to note that high surfactant levels can hinder mass transfer of the solute as the interfacial resistance increases[20]. Similarly, the effect of TEA in the aqueous phase was investigated using different amount of TEA in the aqueous phase. Figure 3(b) shows the stability of emulsion increased from 97 % to 99 % when the concentrations of extractant increased from 2 vol % to 6 vol %. This result suggests that the amount of TEA does not significantly affect the stability of the emulsion. However, it is important to note that the quantity of TEA does influence the absorption of carbon dioxide.

Homogenization time and speed are related to the amount of energy added to produce the emulsion. By adding more energy, smaller droplets are produced. The generation of microsize droplets is important since it provides large surface and thus enhance the transfer of the solute in ELM system of CO2 separation. In this study, the emulsions are prepared by physical shearing process. The ultimate size of a homogenized emulsion is obtained by the balance between two opposing processes; droplet breakup and droplet re-coalescence. During the emulsification, large droplet are initially deformed, elongated and subsequently broken into smaller ones due to shear force applied. Thus, as the homogenization time increases, the size of the droplets decreases, more stable emulsion formed.

The effect of homogenization time and speed on the stability of the emulsion is presented in Fig. 4. For 1 hour stirring, the stability of the emulsion is 88 %, however the stability increases up to 97 % after the emulsion was stirred for 3 hours. As the time increases, it leads to the reduction of the droplet size and improve the homogeneity of the dispersed phase[21]. However, if the homogenization time is too long, the temperature will increases that leads to larger particles and will eventually breakup. The study on the effect of stirring speed showed that at 20,000 rpm, the stability of the emulsion is 97 %. High shear force that acts on the emulsion reduced the size of the droplets, thus increase the stability of the emulsion. However, further increase the speed may increase the osmotic swelling, and thus reduce the stability of the emulsion[21]. Thus, optimum formulation and suitable homogenation time and speed are important to produce a stable emulsion for effective removal of carbon dioxide.

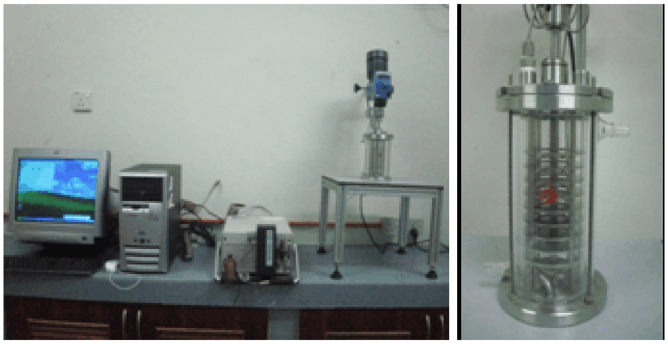


Fig. 1: Experimental apparatus: rotating disc contactor (RDC) column.

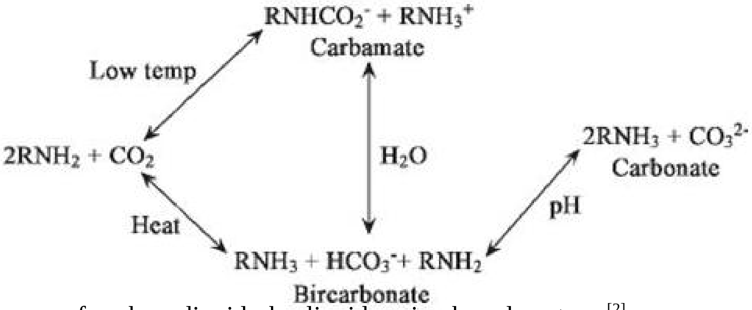
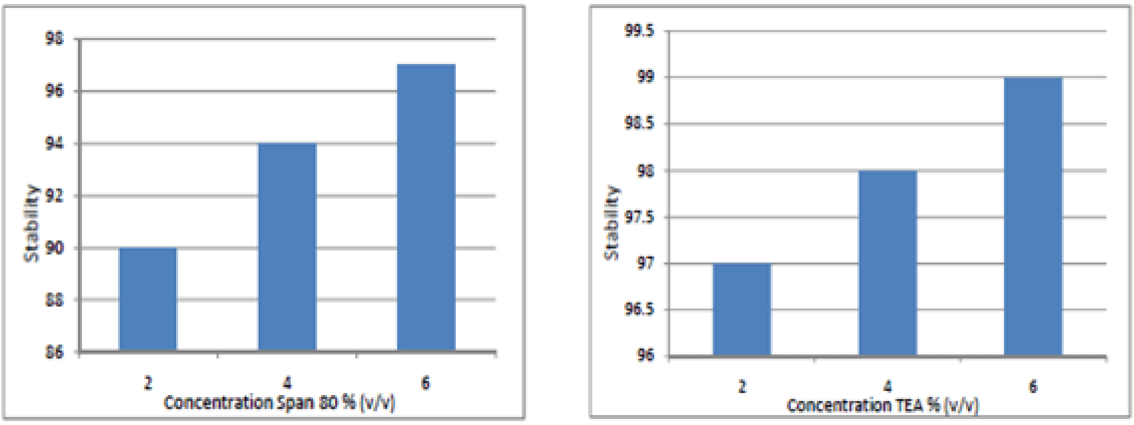


Fig. 2: Reaction sequence of carbon dioxide by liquid amine-based systems[2].



(a) (b)

Fig. 3: Stability of the emulsion (a) Effect of Span 80 (a) Effect of TEA

The removal of carbon dioxide using the emulsion liquid membrane was assessed by determining the amount of carbon dioxide exit from the RDC column. Carbon dioxide was flowed into the rotating disc contactor at the rate of 1 L/hr containing the liquid emulsion. The rotor speed is kept constant at 500 rpm to ensure a good mixing between the emulsion and the dissolved carbon dioxide. The gas-liquid mass transfer rate increased at high rotating speeds resulting from the formation of thinner film or membrane and small droplets[22]. In addition, the presence of TEA enhanced the absorption of the carbon dioxide, thus increase the percentage of carbon dioxide removal from the gas phase. Figure 5 shows the removal of carbon dioxide in the RDC column. The system is found to be stable and can remove up to 87 % of carbon dioxide by using only 6 vol % of TEA in the aqueous phase of the emulsion liquid membrane system. The result indicates that the emulsion liquid membrane system has a potential for removing carbon dioxide using small

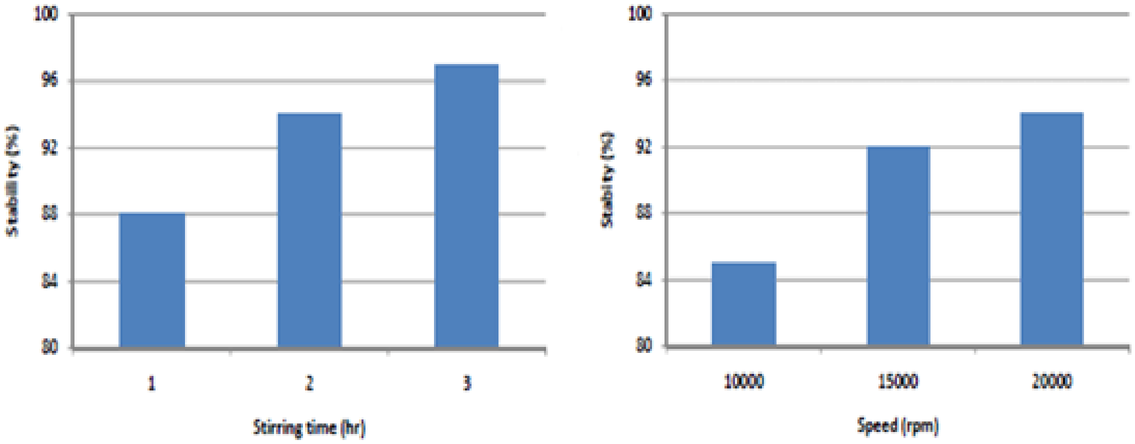


Fig. 4: Effect of homogenization time and speed on the stability of the emulsion liquid membrane.

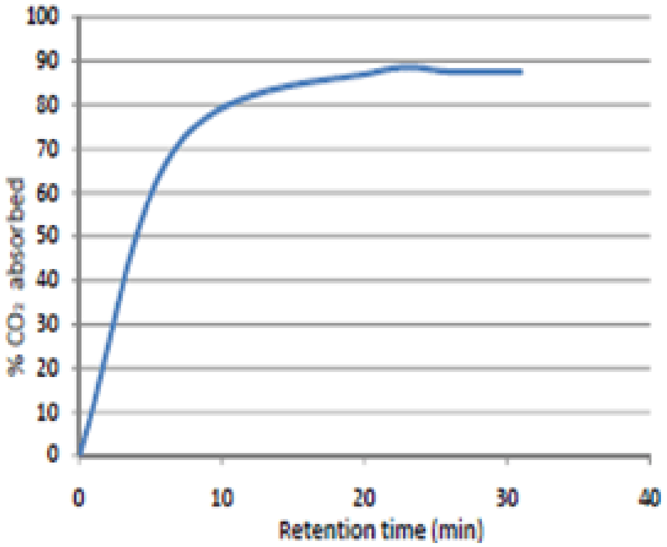


Fig. 5: The percentage of carbon dioxide absorbed in the rotating disc contactor

amount of amine as an extractant. The emulsion liquid membrane also reduce the corrosion problem since droplets containing TEA are dispersed in the organic phase, thus no contact between the amine and the metal surfaces.

Conclusion: The absorption of carbon dioxide into emulsion liquid membrane containing TEA was studied experimentally. It was found by that using 6 vol % of TEA in the aqueous phase, 87 % of carbon dioxide can be removed. It is due to its good reaction with the dissolved carbon dioxide to form bicarbonate or carbamate. In addition, stirring at 20,000 rpm for 3 hours assures a more uniform dispersion of the internal phase that produced a stable emulsion. Therefore, absorption in a water-in-oil emulsion technique can be an alternative method for carbon dioxide removal and overcome the corrosion problem due to corrosive characteristics of the amine.

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REFERENCES

1. Mandal B. and S.S. Bandyopadhyay, 2006. Simultaneous Absorption of CO2 and H2S into Aqueous Blends of N-Methyldietanolamine and Diethanolamine. Environmental Science Technology, 40: 6076-6084.

2. Gray M.L., Y. Soong, K.J. Champagne, H.

Pennline, J.P. Baltrus, R.W. Stevens, R.Jr. Khatri, S.S.C. Chuang and T. Filburn, 2005. Improved Immobilized Carbon Dioxide Capture Sorbents. Fuel Processing Technology, 86(14-15): 1449–1455.

3. Meisen, A. and X.S. Shuai, 1997. Research and Development Issues in CO_2 Capture. Energy Conversion and Management. 38: 837-842.
4. Daiminger, U., W. Lind and M. Mitariten, 2004. Adsorption Added Value. Hydrocarbon Engineering. VII. 2: 83-86.
5. Xu, X., C. Song, B.G. Miller and A.W. Scaroni, 2005. Adsorption Separation of Carbon Dioxide from Flue Gas of Natural Gas-Fired Boiler by A Novel Nanoporous “Molecular Basket” Adsorbent. Fuel Proceeding. Technology, 86: 1457-1472.
6. Lee, C.J. and C.C. Chan, 1990. Extraction Of Ammonia From A Dilute Aqueous Solution By Emulsion Liquid Membranes. 2. Theory And Mass-Transfer Model. Industrial & Engineering Chemistry Research, 29(1): 101-105.
7. Leal-Calderon F., O. Mondain-Monval, K. Pays, N. Royer and J. Bibette, 1997. Water-in-oil Emulsions: Role Of The Solvent Molecular Size On Droplet Interactions. Langmuir, 13: 7008-7011.
8. Kawakatsu T., G. Tragardh, Ch. Tragardh, M. Nakajima, N. Oda and T. Yonemoto 2001. The Effect Of The Hydrophobicity Of Microchannels And Components In Water And Oil Phases On Droplet Formation In Microchannel Water In Oil Emulsification. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 179: 29-37.
9. Skurtys O. and J.M. Aguilera 2009. Formation of O/W Macroemulsions With A Circular Microfluidic Device Using Saponin And Potato Starch. Food Hydrocolloids, 23: 1810-1817.
10. Kumbasar, R.A., 2009. Separation and Concentration Of Cobalt From Aqueous Thiocyanate Solutions Containing Cobalt-Nickel by Emulsion Liquid Membranes Using TBP as Extractant. Journal of Membrane Science, 338: 182-188.
11. Surh J., G.T. Vladisavjevic, S. Mun and D.J. McClements 2007. Preparation and Characterization of Water/Oil and Water/Oil/Water Emulsion Containing Biopolymer-Gelled Water Droplets. Agricultural and Food Chemistry, 55: 175-184.
12. Chakraborty, M. and H.J. Bart, 2006. Emulsion Liquid Membranes: Role of Internal Droplet Size Distribution on Toluene/n-Heptane Separation. Colloids and Surfaces A: Physicochemical Engineering Aspects, 272: 15-21.
13. Fingas M., B. Fieldhouse and J. Mullin, 1995. Water-in-Oil Emulsions: How They Are Formed and Broken. Proceeding International Oil Spill Conference, Long Beach, California.
14. Zwanikken J., J. Graaf, M. Bier and R. van Roij, 2008. Stability of Additive-Free Water-in-Oil Emulsions. Journal of Physics: Condensed Matter, 20: 494238.
15. Abou-Nemeh, I. and A.P. van Peteghem, 1992. Kinetic Study of The Emulsion Breakage During Metals Extraction by Liquid Surfactant Membranes (LSM) From Simulated And Industrial Effluents. Journal of Membrane Science, 70(1): 65-73.
16. Szpakowska, M., 1996. Coupled Transport of Copper Through Different Types of Liquid Membranes containing Acorga P-50 as Carrier. Journal of Membrane Science, 109: 77-86.
17. Park, H.B., Y.K. Kim, J.M. Lee, S.Y. Lee and Y.M. Lee, 2004. Relationship Between Chemical Structure of Aromatic Polyimides and Gas Permeation Properties of Their Carbon Molecular Sieve Membranes. Journal of Membrane Science, 229(1-2): 117-127.
18. Liu W., D. Sun, C. Li, Q. Liu and J. Xu, 2006. Formation and Stability of Faraffin Oil-in-Water Nanoemulsions Prepared by Emulsion Inversion Point Method. Journal of Colloids and Interface Science, 303: 557-563.
19. Leong T.S.H., T.J. Wooster, S.E. Kentish and M. Ashokkumar, 2009. Minimising Oil Droplet Size using Ultrasonic Emulsification. Ultrasonic Sonochemistry, 16: 721-727.
20. Nakashio, F., M. Goto, M. Matsumoto, J. Irie and K. Kondo, 1988. Role Of Surfactants In The Behavior Of Emulsion Liquid Membranes - Development Of New Surfactants. Journal of Membrane Science, 38(3): 249-260.
21. Djenouhat M., O. Hamdaoui, M. Chiha, M.H. Samar, 2008. Ultrasonication-Assisted Preparation of Water-In-Oil Emulsion and Application to the Removal of Cationic Dyes from Water by Emulsion Liquid Membrane Part 1: Membrane Stability. Separation and Purification Technology, 62: 636-641.
22. Tan C.S and J.E. Chen, 2006. Absorption of Carbon Dioxide with Piperazine and Its Mixtures in a Rotating Packed Bed. Separation and Purification Technology, 49: 174-180.