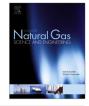
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Mathematical modeling of carbon dioxide removal using amine-promoted hot potassium carbonate in a hollow fiber membrane contactor



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ABSTRACT

In this study, a mathematical model has been developed for absorption of carbon dioxide into promoted hot potassium carbonate in hollow fiber membrane contactors (HFMC). The model, which is based on a conventional split flow absorber (CSFA) unit data of Shiraz Petrochemical Complex, has been validated with the experimental data obtained from literature for CO_2 absorption in MEA promoted NaOH solution as a solvent. The model prediction of carbon dioxide absorption in HFMC has been compared with CSFA. The results indicated that HFMC can be used as an industrial alternative for CO_2 absorption. Absorption of CO_2 in promoted hot potassium carbonate is simulated and compared with N-methyldiethanolamine (MDEA), diethanolamine (DEA), 2–amino–2–methyl–1–propanol (AMP) and aqueous blend of DEA and MDEA. The results represented that the performance of various absorbent solutions for CO_2 removal is as follows: Promoted hot potassium carbonate > AMP > DEA > MDEA > blend of MDEA and DEA. Also investigation of related parameters in carbon dioxide absorption indicated that the removal efficiency enhances with increasing liquid velocity, number of fibers, temperature and also decreasing gas velocity in the membrane contactor.

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1. Introduction

A major greenhouse gas source is CO₂ emission from combustion of fossil fuels such as oil, natural gas, and coal which leads to global warming and climate change (Nalbandian et al., 2011). Environmental considerations represented that the carbon dioxide emission in the European Union (EU) in 2010 increased 3–4% with respect to 1999 (Hammond et al., 2011). So the laws were enacted to reduce carbon dioxide emission throughout the world. The Kyoto protocol and the European Union emission trading scheme are of these laws (Baciocchi et al., 2006). Recently researchers have turned their attention to carbon dioxide capture and storage (CCS) techniques (Rahimpour et al., 2010, Rahimpour and Alizadehhesari, 2009; Baniadam et al., 2009; Haszeldine, 2009; Schrag, 2007; Yuan et al., 2007). These techniques include separation, transportation and storage of concentrated stream of CO₂ for industrial applications (Herzog, 2011). Several methods have been developed for CO₂ capturing. Some of these methods include: post–combustion, pre–combustion, gas hydrates formation, chemical looping combustion and chemical absorption (Figueroa et al., 2008). Most of the mentioned methods have difficulties such as requiring huge amount of energy and expenditure (Rahimpour et al., 2012; Jerndal et al., 2006). Two major drawbacks of absorption tower as a traditional method are the high energy consumption and the equipment size. Also some operational problems such as foaming, channeling, entraining, flooding, etc. exist in these technologies (Al–Marzouqi et al., 2008).

Nowadays application of membranes has been considered by many researchers. Hollow fiber membranes (HFM) are used more than other types of membranes due to its high surface to volume ratio. Hollow fiber membrane has two ducts at the middle of which stands the membrane and fluids flow through the ducts for separation. Since membrane is located between fluids as a solid phase, gas mixture and absorbent liquid are in contact with each other without getting mixed, so increase in the fluid velocity through the

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hollow fiber membranes will not have the common problems of absorption towers (Sohrabi et al., 2011). Moreover hollow fiber membranes have other advantages such as: compact size, easy installation and low cost (Kim and Yang, 2000; Kumar et al., 2002).

Undergone several developments, membranes were employed commercially in the gas separation technology in the 1980s for the first time (Baker, 2002). Absorption capacity of hollow fiber membrane contactor (HFMC) is about 30 times more than usual gas absorption equipment (Cussler, 1994). Qi and Clusser were the pioneers using micro–porous polypropylene membranes for CO₂ absorption (Cussler, 1994; Qi and Cussler, 1985).

Despite all the advantages of membrane technology, there are some limitations such as low permeability and selectivity. These limitations have prevented the wide commercial application of membranes in industrial scale. Therefore, many researchers have tried to overcome the problems of the membranes. Liquid flow rate is an important parameter which determines the selectivity in the membranes (Lv et al., 2012). There are three different modes of membrane pores for separation of components in the gas phase by solvent: wetting, partial-wetting and non-wetting modes. When the membrane pores are completely filled with liquid or gas phase, they are called wetting and non-wetting modes, respectively. The partial wetting mode occurs when there exist both liquid and gas phases in the membrane pores. In the non-wetting mode, mass transfer rate is so higher than other modes (Rahbari-Sisakht et al., 2012). In addition, the material used for making the membranes should have high permeability of gas, high stability, low cost and also the ability to accomplish non-wetting mode. But stability is the most important factor for selection of membrane materials (Porcheron et al., 2011).

Choosing appropriate solvent is another factor which plays an important role in performance of membranes. Many theoretical and experimental studies are carried out to remove CO₂ using different solvents in various hollow fiber membrane contactors (Lv et al., 2012). Zhang et al. (2006) studied carbon dioxide absorption with diethanolamine (DEA) in the hollow fiber membrane. Boucif et al. (2008) comprised carbon dioxide absorption with three alkanolamines. They used diethanolamine (DEA), 2-amino-2methyl-1-propanol (AMP), and diisopropanolamine (DIPA) in their work. Their simulation results have shown that CO₂ absorption would increase when AMP solution is used. Rajabzadeh et al. (2009) experimentally examined the absorption of pure CO₂ into monoethanolamine (MEA) solutions. Their experiment showed that the increase of MEA concentration to 2 mol/m³ would cause increase in the amount of CO₂ removal, whereas further increasing the MEA concentration would hardly enhance the CO₂ absorption flux. Mansourizadeh et al. (2010) considered the CO₂ absorption with aqueous NaOH solution through porous polyvinylidene fluoride (PVDF) hollow fiber membranes. Their results showed when water is used (physical absorption) for CO₂ absorption, any increase in CO₂ pressure or decrease in absorbent temperature would bring about CO₂ flux enhancement. However, in the case of chemical absorption with NaOH (1 M), the results illustrated that the CO₂ flux significantly increase by enhancing the absorbent temperature. In another related study, Al-Marzouqi et al. (2008) developed a twodimensional mathematical model for carbon dioxide absorption. The model was considered partial and complete wetting conditions. In their study, NaOH and MEA solution were used for carbon dioxide absorption. Alkanolamine solutions like monoethanolamine (MEA), diethanolamine (DEA), methyldiethanolamine (MDEA) or hot potassium carbonate have been suggested as the good solvents for CO₂ removal (Todinca et al., 2007; Yan et al., 2008). Hot potassium carbonate was used for CO₂ absorption in the 1950s by Benson et al. (1956), for the first time. Carbonate solutions have high chemical solubility of CO₂ and low costs to the above solvents. However, reaction rate of it in the liquid phase is so slow and the reaction rate could be increased with addition of a promoting agent (Benson et al., 1954). Amine promoted carbonate provides an excellent situation for CO₂ absorption (Rahimpour and Kashkooli, 2004; Olof Nord et al., 2009).

Lee et al. (2001) studied absorption of carbon dioxide using potassium carbonate solution in the hollow fiber membrane for determination of optimal absorbent flow rate. Dindore et al. (2005) have described the effect of aqueous carbonate potassium on the carbon dioxide and hydrogen sulphide absorption in the case of a crossflow membrane contactor. Investigation of CO₂ transfer in an aqueous potassium carbonate liquid membrane module with dense polymeric supporting layers was done by Shalygin et al. (2008). Rahimpour and Kashkooli (2004) studied the effect of promoted hot potassium carbonate on CO₂ absorption in a conventional split flow absorber (CSFA). However, as stated above, the tower will have a number of disadvantages.

This study aims to develop a two dimensional mathematical model for separation of CO₂ from multi component gas mixture by hollow fiber membrane contactor (HFMC). The characteristics of gas and liquid input streams of the hollow fiber membrane are the same as the feed of absorber tower of Shiraz Petrochemical Complex (Rahimpour and Kashkooli, 2004). In this study, application of promoted hot potassium carbonate solution is suggested for carbon dioxide absorption. Diethanolamine (DEA) is a promoter agent to increase the reaction rate of potassium carbonate with CO₂. This research attempts to compare carbon dioxide absorption in HFMC and CSFA. Also carbon dioxide absorption via various solvents (DEA. MDEA, AMP, aqueous blends of DEA and MDEA, and promoted hot potassium carbonate) in HFMC is investigated. The comparison is done by considering different parameters such as change of initial carbon dioxide concentration, gas and liquid flow rates, number of fibers and temperature.

2. Process description

2.1. Conventional split flow absorber (CSFA)

Fig. 1 shows a schematic diagram of the split flow absorber tower which is used in Shiraz Petrochemical Complex for CO₂ absorption. The gas mixture which consists carbon dioxide, carbon monoxide, methane, hydrogen, argon and water is fed into the bottom of the absorber column in a countercurrent contacting mode with lean amine promoted hot potassium carbonate solution. Since the input stream of absorbent liquid to the absorption tower is divided into two parts, it is called split flow. A portion of the lean solution passes through a heat exchanger at the entrance of absorber tower for reduction of its temperature. The other part of lean solution directly enters the absorber tower without any change of its temperature. This stream division will cause increase in driving force of mass transfer through the tower. After absorption process, the CO₂ rich solution leaves the absorber and enters the regenerator tower from the top and is stripped by low pressure stream in an opposite direction. Extracted CO₂ is compressed and removed from the top of regenerator column while lean solution is returned to the absorber tower with equilibrium vapor pressure of CO₂ in order to enhance the purity of the produced gas. Rahimpour and Kashkooli (2004) mathematically modeled the packed absorber tower. The properties of absorption and stripper towers of Shiraz Petrochemical Complex are indicated in Table 1.

2.2. Hollow fiber membrane contactor (HFMC)

As shown in Fig. 2, the gas and the liquid flow through two different sides of HFMC with counter–current operation mode and

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