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Mathematical modeling of CO_2 separation from gaseous-mixture using a Hollow-Fiber Membrane Module: Physical mechanism and influence of partial-wetting

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ABSTRACT

The present study describes a steady-state phenomenological model for CO_2 separation via reactive absorption into aqueous Diethanolamine (DEA) solution using a micro-porous Poly-propylene (PP) Hollow-Fiber Membrane Module (HFMM). The developed model is based on the fundamental mechanisms of molecular diffusion, bulk convection and liquid-phase chemical reaction, and simultaneously accounts for the consequences of 'partial-wetting' phenomenon. Furthermore, a physically-consistent wetting mechanism has been formulated assuming that the membrane pores may be modeled as a bundle of straight cylindrical capillaries with distinct radii (characterized by the membrane pore-size distribution) and equal lengths, while keeping in mind the various pore-scale micro-physical phenomena. Under the simplifying parameterizations of the Finite-Volume Method (FVM), the source-code for discretized equations was compiled and implemented using C++ Language for a co-current module operation with aqueous DEA solution flowing inside the fiber-lumen and CO_2–N_2 gaseous mixture passing through the shell-side. A Benchmarking Analysis revealed an excellent agreement between the model predictions and the experimental data reported in open-literature, thereby validating the current model formulation, and rendering it fundamentally relevant with respect to the wetting-phenomenon. In addition, the module performance in terms of CO_2 flux, Overall Mass-Transfer Coefficient (MTC), and Removal-Efficiency, has been systematically analyzed pertaining to the physical influence of other operating variables such as absorbent concentration, hydrodynamics, pressure, temperature, and membrane characteristics. From a modeling standpoint, it may be concluded that the present model successfully captures various observations vis-à-vis the process of CO_2 separation using micro-porous HFMMs, reported previously in the literature. Moreover, for a given gas-phase hydrodynamics, the current set of results suggest the existence of a unique liquid-phase hydrodynamic regime, bounded by a minimum and a maximum permissible pressure, under which the module can be effectively operated without any dispersive losses. Besides, the currently developed model has been demonstrated to explain the reduction in CO_2 flux over time by allowing for morphological changes, including an enlargement in the average pore-size and a broadening of the pore-size distribution.

1. Introduction

The global carbon emissions have increased considerably in the past three decades, mainly due to our dependence on fossil-fuels to meet our energy requirements. Therefore, novel separation techniques have attracted a lot of attention recently to rein in CO_2, the major greenhouse gas responsible for global warming. Amongst various alternatives, the use of Hollow Fiber Membrane Modules (HFMMs) for chemical absorption into aqueous alkanolamines, represents a high-efficiency method to capture CO_2 [1]. Micro-porous HFMMs provide a higher surface area per unit volume for continuous gas–liquid contact as compared to packed beds and correspondingly high mass-transfer rates. With this behavior staying unviolated in a wide range of flow rates, the common problems of loading and flooding with packed towers can be avoided by the use of HFMMs for CO_2 absorption [2]. However, the phenomenon of gradual membrane wetting by absorbent over longer time-scales increases the overall mass-transfer resistance

Abbreviations: HFMM, Hollow-Fiber Membrane Module; FVM, Finite-Volume Method; MTC, Mass Transfer Coefficient; PP, Polypropylene; TMPD, Transmembrane Pressure Difference

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and needs to be addressed during process intensification studies [3]. Therefore, the choice of membrane material is critical to the efficiency of this process, and preference must be given to hydrophobic polymers like poly-vinylidene-fluoride (PVDF), poly-propylene (PP), poly-tetrafluoro-ethylene (PTFE) and poly-sulfone (PS) in order to avoid membrane wetting.

Numerous modeling and experimental investigations [2–26] have been conducted previously to understand CO_2 separation using HFMMs. The application of PS and PP HFMMs for CO_2 separation was experimentally investigated by Kreulen et al. [4,5]. For the case of physical absorption in water, the authors [4] discussed advantages of HFMMs over traditional bubble-column contactors, the effect of mal-distribution of phases and correlated the results using the heat transfer analog of Graetz–Leveque solution. In a complementary study of chemical absorption in aqueous NaOH, the authors discussed the experimental results in parallel with a mathematical model formulated under the assumption of zero-wetting [5]. Likewise, Yan et al. [6] experimentally demonstrated the use of aqueous Potassium Glycinate (PG) as an absorbent for CO_2 separation using non-wetted PP HFMMs. The process of CO_2 absorption in aqueous Potassium Glycinate (PG) using a PTFE HFMM has been further explored by Eslami et al. [7] through a mathematical model developed using COMSOL software package with non-wetting physics. Similarly, Zhang et al. [8] deployed MATLAB as a mathematical tool to study CO_2 absorption in water and aqueous Diethanolamine (DEA) using PP HFMMs under non-wetting conditions. At this point, one should note that although these studies [4–8] ignored the repercussions of wetting phenomenon, 'partial-wetting' of hydrophobic HFMMs cannot be avoided when the liquid-phase pressure is higher than its gas-phase counterpart, a primary condition that must be met in order to avoid any hydrodynamic inter-dispersion of the two phases [9,10].

Over the years, several authors [11–20] have reported the occurrence of wetting during experimental studies with HFMMs. For instance: refer to the work of Kreulen et al. [11], who determined the mass-transfer resistance of both wetted and non-wetted flat microporous membranes, and attributed the corresponding inconsistencies to the phenomenon of 'partial-wetting'. Analogously, Rangwala [12] studied CO_2 absorption in water, DEA and NaOH using PP HFMMs, and ascribed the discrepancy between the theoretically and experimentally determined MTC values to be an implicit manifestation of 'partial-wetting'. Similar observations of reduction in CO_2 flux owing to the 'partial-wetting' of HFMMs have been discussed by other authors [13–20] as well. A particularly interesting experimental study of CO_2 removal from natural gas at high gas-phase pressures using aqueous Mono-ethanolamine (MEA) was conducted by Faiz and Al-Marzouqi [20] who reported a good agreement with the theoretical predictions corresponding to a 0.5% 'pseudo-wetting'. Although such a small extent of membrane-wetting makes sense, especially with the gas-phase pressure reaching as high as 50 bars, the authors' [20] efforts may possibly be clouded by the complexity of hydrodynamics at such high operating pressures i.e. the overlooked dispersive interactions between the two phases. To appreciate this, one may refer to the work of Kreulen et al. [5], who observed the formation of small gas-bubbles in the liquid-phase on account of an inevitable rise in the gas-phase pressure with increasing velocity.

In light of the aforementioned arguments, it becomes essential to study the potential implications of wetting phenomenon on the module performance under diverse operating conditions. Till date, only a few theoretical and experimental attempts have been made in this regard. Vis-à-vis the assumptions of 'no-wetting' and 'complete-wetting', a mathematical model has been discussed and experimentally validated in the work of Karoor and Sirkar [21] for gas-absorption in water using microporous HFMMs. As to the phenomenon of 'partial-wetting', practically all prior studies [10,16,20,22,23] available under open-literature have suggested the use of a wetting fraction, representative of the extent to which the membrane may be wetted, as a fitting parameter to match the theoretical predictions to experimental results. Distinct from this seemingly dominant perspective, Malek et al. [24] described a mathematical model to analyze dissolved O_2 removal from water using microporous HFMMs under a loose assumption of 'partial-wetting'. Loose in the sense that for points along the fiber length where the transmembrane pressure difference (TMPD) exceeded the critical wetting-pressure (determined by the Laplace Equation), the authors [24] assumed 'complete-wetting' for simulation purposes and a 'no-wetting' mode otherwise. Furthermore, the authors [24] assumed a constant value for the critical wetting-pressure, based on the average pore-size, similar to the work of Rangwala [12], which may not be valid for membranes with a non-uniform pore-size distribution. While distinctively notable attempts [25,26] have been made previously to relax these assumptions, these are restrictive at the same time with respect to a few irregularities. For instance: Lu et al. [25] made efforts to formulate a wetting mechanism by accounting for the influence of transmembrane pressure difference (TMPD), capillary pressure and a log-normal pore-size distribution. However, the expression for the wetting fraction reported by Lu et al. [25] seems mathematically inconsistent vis-à-vis a normalized pore-size distribution, further details of which have been explained later in this study. Their work was succeeded by the work of Boributh et al. [26], who adapted Lu et al.'s mechanism for further mathematical analysis.

Therefore, it is quite evident that despite the several prior attempts, large uncertainties remain in the current state of understanding on wetting phenomenon in HFMMs. Additionally, a combination of multifaceted pore-scale micro-physical phenomena may render the gas–liquid interface immobilized inside membrane pores, thereby causing a 'partial-wetting' of the HFMM. Inclusive attempts, towards the quantification of mass-transfer resistance, prevailing in the membrane under a given set of operating conditions, have not been reported so far in the open-literature. Likewise, the phenomenon of 'partial-wetting' has not been studied in detail, compared to the customary assumptions of 'no-wetting' and 'complete-wetting' reported in earlier studies. The present work is an effort en-route to the mechanistic modeling of reactive CO_2 absorption using aqueous DEA solution in a PP HFMM. A wetting-mechanism, formulated through a physical coupling of the log-normal pore-size distribution along-with the well-established capillary bundle representation of membrane pores, has been described for incorporation into the developed mathematical model. Furthermore, a systematic analysis of the relative importance of different parameters in the determining the module performance: Flux, Overall MTC and Removal Efficiency, has been discussed as a part of a larger effort to quantify the physical effects of hydrodynamics, temperature, pressure, and membrane characteristics.

2. Mathematical model

The schematic of a hollow-fiber with a co-current flow of liquid inside the fiber-lumen and gas through the shell-side is displayed in Fig. 1. The characteristic dimensions of a commercially available HFMM: MiniModule® 1×5.5 Liqui-Cel Membrane Contactor, procured from Membrana (Celgard LLC – Charlotte, USA), described in Table 1, have been used in the current study. The independent formulation of transport model on a single fiber basis requires the shell-side dimensions to be explicitly defined. This is accomplished by use of *Happel's Free-Surface Model* [27] to