CO$_2$ capture in cation-exchanged metal–organic frameworks: Holistic modeling from molecular simulation to process optimization
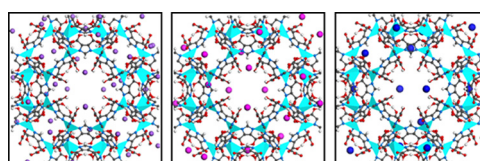
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A. Nalaparaju, M. Khurana, S. Farooq *, I.A. Karimi, J.W. Jiang **

Department of Chemical and Biomolecular Engineering, National University of Singapore, Singapore 117565, Singapore

HIGHLIGHTS

- CO$_2$ capture from dry flue gas is investigated by holistic multi-scale modeling.
- Pure-component adsorption and diffusion data are provided by molecular simulation.
- A four-step vacuum swing adsorption process is simulated and optimized.
- Energy penalty-productivity Paretos are presented for CO$_2$ capture in *rho*-ZMOFs.

GRAPHICAL ABSTRACT

ABSTRACT

While CO$_2$ capture has been extensively investigated in different metal–organic frameworks (MOFs), their performance under practical process conditions is scarcely examined. In this study, a multi-scale modeling study is reported to examine CO$_2$ capture from flue gas by vacuum swing adsorption (VSA) process using cation-exchanged *rho* zeolite-like MOFs (*rho*-ZMOFs) as adsorbents. Three *rho*-ZMOFs namely Na-, Mg- and Al-*rho*-ZMOFs are considered and compared with 13X Zeolite, which is the current benchmark for post-combustion capture from dry flue gas. First, Monte Carlo (MC) simulations are conducted to estimate the adsorption isotherms of pure CO$_2$ and N$_2$ in the range from 0 to 100 kPa and their mixtures of varying composition at a total pressure of 100 kPa. The pure gas isotherms are then fitted by the dual-site Langmuir model. Subsequently, the extended dual-site Langmuir model is used to satisfactorily predict the equilibrium behavior of CO$_2$/N$_2$ binary mixtures over a wide range of composition. In addition, micropore diffusivities are calculated from molecular dynamics (MD) simulations and compared with the estimated macropore diffusivities in order to determine the controlling mechanism of mass transfer. Macropore is expected when these adsorbents are pelletized before using in a separation process. For each *rho*-ZMOF adsorbent, a four-step VSA process with light product pressurization for CO$_2$ capture and concentration (CCC) from dry flue gas containing 15% CO$_2$ in balance N$_2$ is then simulated using a non-isothermal, non-isobaric model. The process is optimized using multi-objective optimization based on a genetic algorithm for minimizing the energy penalty and maximizing the process productivity, subject to the purity and recovery constraints of 95 and 90%, respectively. The operating spaces of the three *rho*-ZMOFs are similar to that of 13X zeolite. However, the minimum energy penalty in Al-*rho*-ZMOF (156 kW h/t CO$_2$) is lower than in 13X (165 kW h/t CO$_2$). While identifying the cation-exchanged *rho*-ZMOFs as interesting candidates for CO$_2$ capture, this study also demonstrates that the multi-scale modeling approach adopted here is an effective methodology to screen and design novel MOFs for CCC and other separation applications.

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* Corresponding author. Tel.: +65 65166545; fax: +65 67791936.
** Corresponding author. Tel.: +65 65165083; fax: +65 67791936.
  E-mail addresses: chesf@nus.edu.sg (S. Farooq), chejj@nus.edu.sg (J.W. Jiang).

1. Introduction

Flue gas from fossil-fuel power plants accounts 33–40% of global CO_2 emissions (Yang et al., 2008). The emissions are expected to increase because cheap and abundant fossil fuels will continue to be a substantial fraction of energy portfolio in the foreseeable future. There is an urgent need to reduce carbon footprint for environmental protection and sustainable development. Flue gas is primarily composed of N_2 and a relatively lower concentration of CO_2, and the separation of CO_2/N_2 is a crucial step prior to CO_2 sequestration or conversion. In a typical CO_2 capture and sequestration process, CO_2 capture alone represents 70–80% of total cost. Therefore, the development of a cost-effective approach for CO_2 capture has attracted considerable interest.

Currently, the most widely practiced technique for CO_2 capture is amine scrubbing using aqueous alkanolamine solutions (Haszeldine, 2009). However, the process is plagued with corrosion and high energy consumption in solvent regeneration. Adsorption based CO_2 capture process offers a technically feasible and economically viable alternative (Ho et al., 2008). To carry out adsorptive separation, pressure swing adsorption (PSA) with several fixed-beds is often implemented. PSA requires a high-performance adsorbent with large capacity, high selectivity and easy regeneration. While a variety of adsorbents have been tested for CO_2 separation from flue gas, such as carbonaceous and zeolitic materials, they are either not sufficiently selective or difficult to be regenerated (Aaron and Tsouris, 2005). Thus, there is a continuous quest to develop novel adsorbents for CO_2 capture.

In the last decade, metal–organic frameworks (MOFs) have emerged as a new class of porous materials with unique features, such as large surface area (up to 7140 m^2/g) and high porosity (up to 90%) (Furukawa et al., 2013). MOFs are assembled from metal clusters (e.g. square-shaped, trigonal, tetrahedral and octahedral) and organic linkers (e.g. carboxylates, imidazolates and tetrazolates). By judiciously tuning metals and linkers, nearly unlimited MOFs with different structures and functionalities can be synthesized. Consequently, MOFs have been considered as versatile materials potentially for storage, separation, catalysis and biomedical applications (Férey, 2008; Zhou et al., 2012). To date, a larger number of experimental and simulation studies have been reported for CO_2 adsorption and separation in various MOFs (Sumida et al., 2012; Jiang, 2012). Nevertheless, they were mostly focused on CO_2 capacity and selectivity from a material perspective, or breakthrough behavior in a single adsorption column. Bastin et al. (2008) reported CO_2 separation from CO_2/N_2 and CO_2/CH_4 mixtures in a fixed-bed with a microporous MOF. Xiang et al. compared several MOFs for CO_2 capture based on uptake, selectivity, as well as breakthrough measurement, and suggested that UTSA-16 is a potentially useful absorbent (Xiang et al., 2012). Sabouni et al. (2013) examined the effects of operation conditions on CO_2 separation in fixed-bed with CPM-5. The ultimate target of materials synthesis/research is desirable process performance, which however is scarcely reported for MOFs.

In this study, the synergy of a multi-scale modeling approach, from molecular simulation to process optimization is proposed to investigate CO_2 capture from flue gas using MOFs. Given the modular nature and large number of possible MOF structures, it is infeasible to examine them by time-consuming and costly experiments. Computer-based simulation and optimization thus provide a reliable next best alternative. Specifically, Monte Carlo simulations are first conducted to obtain equilibrium isotherms in MOFs. Molecular dynamics simulations are then performed to determine mass transfer properties. Subsequently, the equilibrium and kinetic data obtained from molecular simulations are used to perform process simulations for these adsorbents. The process is finally optimized to achieve minimum energy penalty and maximum productivity for the respective adsorbents, which are then compared on the basis of their process performances.

The MOFs considered are cation-exchanged *rho*-zeolite like MOFs (*rho*-ZMOFs) (Liu et al., 2006), with high chemical and thermal stability. Due to the presence of cations, *rho*-ZMOFs were found to exhibit high CO_2 uptake and selectivity (Babarao and Jiang, 2009; Chen et al., 2012). However, it remains unknown how these intriguing MOFs would perform in a practical PSA process for CO_2 capture, which is the objective of this study. Following this introduction, molecular simulations of the adsorption of pure CO_2 and N_2 and their mixture, and diffusion of these two gases in *rho*-ZMOFs are described in Section 2. The adsorption properties of pure CO_2 and N_2 in Na-, Mg- and Al-*rho*-ZMOFs from simulation are presented and the effect of cations on adsorption is discussed. In Section 3, the equilibrium isotherm model and transport mechanism of CO_2 and N_2 adsorption in *rho*-MOFs are presented. The dual-site Langmuir model is used to fit the simulated isotherms. For CO_2/N_2 binary mixtures, the simulated adsorption isotherms and selectivities are compared with predictions from the extended dual-site Langmuir model. Then, the roles of micro- and macropore resistances in mass transfer are examined. In Section 4, a four-step VSA process is optimized for the *rho*-ZMOFs. The energy-productivity Paretos in the *rho*-ZMOFs are shown and compared with 13X. Finally, the concluding remarks are summarized in Section 5.

2. Molecular simulation of adsorption and diffusion

The *rho*-ZMOF represents the first example of 4-connected MOF with *rho* topology. It was synthesized by the directed assembly of In atoms and 4,5-imidazoledicarboxylic acid (H_3ImDC) (Liu et al., 2006). The substitution of oxygen in *rho*-zeolite by doubly deprotonated H_3ImDC (HImDC) generates an open structure with large truncated cuboctahedra (α-cages) of 18.2 Å in diameter. Unlike *rho*-zeolite, *rho*-ZMOF possesses twice as many positive charges (48 vs. 24) in a unit cell to neutralize the anionic framework. The parent *rho*-ZMOF contains doubly protonated 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine (HPP), which can be exchanged with other cations. In this study, Na-, Mg- and Al-*rho*-ZMOFs are examined to represent monovalent, divalent and trivalent cation-exchanged samples. Their atomic structures are illustrated in Fig. 1, in which the equilibrium locations of cations were determined by simulated annealing method (Chen et al., 2012; Babarao and Jiang, 2009). The atomic charges of the framework atoms were calculated by density functional theory (DFT) using a fragmental cluster (see Fig. S1 in the supplementary data). The DFT calculations used the Becke's three-parameter exchange functional with Lee–Yang–Parr nonlocal correlation (B3LYP) and were carried out using Gaussian 03 package (Frisch et al., 2004). Moreover, 6–31G(d) basis set was used for all the framework atoms except In, for which LANL2DZ basis set was used. The concept of atomic charges is solely an approximation and no unique straightforward method is currently available to rigorously determine atomic charges. In this study, the atomic charges were estimated by fitting to the electrostatic potentials (ESP). The dispersive interactions of framework atoms and cations were modeled by the Universal Force Field (UFF) (Rappe et al., 1992), as listed in Table 1. A number of simulation studies have shown that UFF can accurately predict gas adsorption in various MOFs (Babarao and Jiang, 2008; Chen and Jiang, 2010; Skoulidias and Sholl, 2005; Garberoglio et al., 2005).

CO_2 was modeled by a three-site rigid molecule, in which the partial charges on C and O atoms were $q_C = 0.576e$ and $q_O = -0.288e$ ($e = 1.6022 \times 10^{-19}$) (Hirotani et al., 1997). The C–O bond length was 1.18 Å and the bond angle $\angle OCO$ was 180°. N_2 was represented