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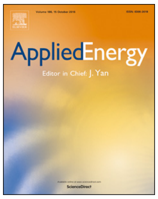

Adsorption breakthrough and cycling stability of carbon dioxide separation from $CO_2/N_2/H_2O$ mixture under ambient conditions using 13X and Mg-MOF-74

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HIGHLIGHTS

- Adsorption separation of CO_2 from dry and humid CO_2/N_2 mixture is carried out under ambient conditions.
- Experimentally validated model is applied by a user-defined-function in ANSYS Fluent.
- 13X and Mg-MOF-74 are tested for breakthrough and cyclic CO_2 separations.
- Dehydration process before CO_2 adsorption processes is strongly recommended.
- Cycling separation is recommended to be used instead of breakthrough tests.

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ABSTRACT

Carbon dioxide and storage is an efficient method to reduce the emitted CO_2 from the burning of fossil fuels. Zeolite-based materials are conventional adsorbents used to adsorb some gasses involving carbon dioxide. Mg-MOF-74 is an eminent reticular material among adsorbents due to its good CO_2 capacity at low pressures (10–20 kPa). In this study, an experimentally validated model is used to report the H_2O effect on CO_2 separation using 13X and Mg-MOF-74 under ambient conditions. A computational model has been developed using ANSYS Fluent program linked by user-define-function (written in C). The adsorption breakthrough results show that a humid CO_2/N_2 mixture, under 300 K, 86% RH, 101.3 kPa, could slightly reduce the CO_2 adsorption capacity by about 0.05% and 6% for 13X and Mg-MOF-74, respectively (at CO_2 adsorption breakthrough saturation). Regardless of these reductions, Mg-MOF-74 has better adsorption capacity, even under humid ambient conditions, by about 5.77 mmol/g in a comparison to 2.27 mmol/g for 13X, respectively.

Cycling stability over more than 90 cycles is also simulated; and shows that, a dehydration process is recommended to be carried out before the CO_2 separation process for efficient energy consumption and sustainable adsorbents. The total recyclable amounts of adsorbed CO_2 are about 0.94 and 3.07 mmol/g for 13X and Mg-MOF-74, respectively, under 101.3 kPa adsorption, 2 kPa desorption, 86% relative humidity, and 298 K. The cyclic CO_2 separation is found to be a robust method more than the breakthrough separation to evaluate the real adsorption capacities.

1. Introduction

CO_2 separation by the adsorption technologies is growing vastly. The utmost advantage of the adsorption separation processes is the simplicity of adsorbent regeneration by means of heat, vacuum or both [1]. Carbon- and zeolite-based adsorbents are well-known materials exploited for the CO_2 separation. In particular, zeolite-based adsorbents show better CO_2 uptakes than activated carbons under lower operating pressures (10–20 kPa) such as NaY, 13X [2], and CNT/13X [3], whereas carbon-based adsorbents are preferred under high pressures (CO_2 adsorptive storage pressures > 5 bar) [4]. Metal-organic frameworks (MOFs) are a new class of novel adsorbents [5]. Specifically, MOF-74 (e.g., MOF-74(Ni, Co) [6] and MOF-74(Mg) [7]) shows a good CO_2 adsorption capacity and CO_2 over N_2 selectivity. Quantitatively, Mg-MOF-74 was tested to have the highest CO_2 adsorptive capacity under low-pressure conditions (350 mg/g at 298 K and 1 bar) [7].

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Nomenclature

C	molar concentration of gas, mol/m^3
C_p	specific heat capacity, J/kg·K
D, d	bed diameter, particle-size, m
D_{disp}	coefficient of gas dispersion, m^2/s
E_g	energy of gas-phase, J/m^3
E_s	energy of solid-phase, J/m^3
h	enthalpy, J/kg
h_{ext}	coefficient of heat transfer at outer bed surface, W/m^2·K
h_{int}	coefficient of heat transfer at internal bed surface, W/m^2·K
ΔH	adsorption heat, J/mol
$\vec{g}$	acceleration vector of gravity, m/s
$\vec{J}$	flux due to diffusion, kg/m^2·s
K_o	constant in Toth equation, 1/Pa
K_{eq}	constant in Toth equation, 1/Pa
k	thermal conductivity, W/m·K
k_L	time constant of LDF, 1/s
M	mass weight, kg/mol
n	constant in Toth equation
q	actual adsorbed gas, mmol/g
q^*	equilibrium adsorbed gas, mmol/g
q_m	capacity limit, mmol/g
Q_F	inlet flow rate, m^3/s
P	pressure, Pa
R	universal gas constant, J/mol·K
r	radius, m
Re	Reynolds number
t	time, s
T	operating temperature, K
$\bar{\bar{\tau}}$	stress tensor, N/m^2
y	weight fraction
$\vec{v}$	velocity, m/s

Greek letters

ρ	gas density, kg/m^3
ε	porosity of adsorbent bed
γ	heat capacity ratio
ε	thermal emissivity
μ	dynamic viscosity, Pa·s
η	vacuum pump efficiency
σ	Stefan Boltzmann coefficient, W/m^2·K^4
τ	tortuosity

Subscripts

eff	effective
p	particle
max	maximum
min	minimum
pore	pore od adsorbent
i	species index of gas
g	gas
s	standard conditions
0	inlet, saturation
w	wall

1.1. CO_2 separation under humid conditions

Many studies have been conducted on developing water-stable adsorbents to be used in the CO_2 capture processes [8]. Some materials showed a significant reduction in the CO_2 adsorption in the presence of water while others were stable. It is found that CO_2 recovery was minimized by 22% using 13X under 95% RH, 30 °C, and 1.2 bar [9]. However, 13X has been tested and showed an excellent stability under humid conditions [10]. The structural stability tests under humid conditions (298 K and RH $<$ 90%) showed that HKUST-1, Mg-MOF-74, and UiO-66 (−$NH_{2)}$ retained a good structuration while DMOF-1, DMOF-1-NH_2, and UMCM-1 were not stable and completely lost their crystallinity [11]. A negligible drop in CO_2 uptake was observed by testing HKUST-1 and Ni/DOBDC under humid conditions [12]. MOF-841 was, also, reported as a water and cycling stable adsorbent [13].

Despite the high CO_2 uptake of Mg-MOF-74, the presence of H_2O reduced the CO_2 capture capacity, unlike some MOFs such as HKUST-1 and MIL-101(Cr) [14]. For example, at 1 bar and 298 K, about 8.4 mmol/g CO_2 could be adsorbed by dry Mg-MOF-74; while under hydration of 6.5% and 13%, about 6.7 mmol/g and 5.4 mmol/g CO_2 could be adsorbed, respectively [14]. It is also reported that Mg-MOF-74 has higher H_2O hydrophilicity (593 mL/g at 298 K and 1 bar) than zeolite [15]. The reduction of CO_2 uptake at 373 K, 9% RH, and 101.3 kPa was addressed to be about 47% using Mg-MOF-74 [16].

The functionalization of MOFs by amine groups showed a higher CO_2 uptake under H_2O presence than those under dry conditions [17]. Amine-impregnated silicic acid composite was introduced as a candidate adsorbent for CO_2 separation having a CO_2 uptake of 4.54 mmol/g at 25 °C under 10 vol% CO_2 and 10 vol% H_2O [18]. Polyethyleneimine-(PEI)-impregnated millimeter-sized mesoporous carbon spheres (MCSs) showed an excellent stability for CO_2 capture in the presence of H_2O [19]. KFUPM-1 (polymer-adsorbent treated by amine-group) showed a higher cyclic stability and CO_2 uptake under the presence of water vapor [20]. About 0.75 cyclic CO_2 uptake was achieved using CaO/MgO (calcium-based adsorbent) under real conditions [21]. Recently, some adsorbents were proposed to be water-stable for CO_2 post-combustion such as dmpn-Mg_2(dopbpdc) [22], NbOFFIVE-1-Ni [10], nHept-2– Mg_2(pc-dobpdc) [23], IRMOF-74-III-$(CH_2NH_2)_2$ [24], and ZIF-300 [25]. Notwithstanding that some MOFs exhibit water and thermal stability, there are many challenges for such adsorbents to be applicable to commercial and real-world; e.g., combining high CO_2 capacity with high CO_2/N_2 selectivity in the presence of humidity [8].

1.2. Energy consumption by carbon capture processes

The energy penalties due to the separation of CO_2 in power plants were estimated in the literature. The cost of avoiding CO_2, for amine scrubbing plant integrated with natural gas combined cycles, was evaluated to be between \$82.6 and \$121.8 per tonne of CO_2 [26]. Bicarbonate-forming solvents could also be used for carbon capture with CO_2 avoid energy about 0.27 kWh/kg CO_2 [27]. The average annual CO_2 emission rate for the integrated gasification combined cycle (IGCC) integrated with membrane CO_2 capture, was at 89 kg CO_2/MWh [28]. Analogous to thermodynamic cycles, the carbon pump theory was used for investigating thermodynamics and energy consumption of the TSA process [29]. Incorporating secondary materials (such as CNT) with MOFs could increase the CO_2 uptake and decrease the regeneration energy; it is found that the CO_2 uptake increased by 36% for MIL-101(Cr) [30] and about 8% for Mg-MOF-74 [31].

Among different CO_2 separation technologies, the electric adsorption separation process was addressed to be economically infeasible for CO_2 capture [32]. The effect of water vapor on the CO_2 separation using activated carbon (coconut shell Acticarb GC1200) was small, but it has a high impact on the power consumption (~35%) of vacuum swing adsorption process [33]. The energy consumption of CO_2-loaded aqueous amine solution using Al2O3/HZSM-5 bifunctional catalysts was found to be less than a catalyst-free test by 23.3–34.2% [34]. For separating CO_2 from the atmospheric air, the energy consumption was