CO₂ Adsorption in a Geopolymer-Zeolite Composite: Experimental Dynamic Tests and Modelling Insights on Related Thermal Effects

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CO₂ adsorption process in a composite geopolymer/zeolite 13X material has been analysed for post combustion carbon capture application, in dynamic conditions for a CO₂/N₂ gas mixture. Such composite material represents a valid alternative to conventional sorbents owing to the affinity and synergy between zeolite and the geopolymer binder as well as improved mechanical resistance and lower cost. Experimental analysis has been focused both on complete adsorption tests to determine the material maximum adsorption capacity and on breakthrough tests in transient conditions in (cyclic adsorption/desorption). Particular care has been devoted to thermal effects associated to adsorption and their effect on adsorption capacity and kinetics.

Experimental data have been employed to support the development of a novel numerical model, based on Sips adsorption approach for sorbent capacity, and capable to describe the adsorption process, accounting for both mass and energy transport in the sorbent bed. The model proved able to describe well the experimental data at different CO₂ feed concentration, and thus it has been employed in a predictive way to inspect process operating parameters and sorbent bed design on the resulting adsorption capacity, breakthrough time, and temperature profile. In particular, the model compared the results obtained in a scaled-up configuration (suitable to an industrial application) with those of the lab-scale system.

1. Introduction

Carbon capture can be conveniently used to mitigate the greenhouse effect from power plants or industrial production sites such as cement plants. A possible CO₂ separation technique is represented by adsorption onto solid sorbent beds, with the potential to be cost effective and to be retrofitted to existing plants (Younas et al., 2016). Several possible solid sorbents, with various adsorption capacities have been tested for carbon capture applications: MOFs, natural and synthetic zeolites (Ammendola et al., 2020), activated carbons (Vargas et al., 2013), organic polymers, geopolymers (Minelli et al., 2016) and their composites (Samanta et al., 2012). Indeed, sorbent materials should be selected according to their adsorption capacity, selectivity towards other gases, thermal stability and mechanical resistance.

Carbon dioxide adsorption is typically accomplished in a semi continuous process, where the sorbent bed is fed with the CO₂ containing gaseous stream until achievement of breakthrough point, after which the feed is switched to a second bed. The exhausted bed can be regenerated by either increasing the temperature (temperature swing adsorption TSA), or decreasing the pressure (pressure swing adsorption PSA). Breakthrough time is defined as the time required to reach a certain threshold of CO₂ (e.g. 5 % of inlet value) in the outlet stream and can be optimized according to sorbent and operating characteristics to maximize bed

utilization, modifying design and process variables. Continuous operation of sorption processes may instead be achieved with fluidized bed reactors (Gupta and Kumar, 2020).

Adsorption is always accompanied by relevant thermal effects, due to the exothermicity of the process. Such effects may affect sorption dynamics and effectiveness (Xiao et al., 2016). In particular, CO_2 adsorption on zeolites presents isosteric heats in the range of 33 to 41 kJ/mol (Lee et al., 2002; Harper et al., 1969). The heat release can be mitigated with the inclusion of zeolites in a composite material, where the matrix provides high mechanical resistance. In this respect, geopolymers, a class of inorganic amorphous materials, have been employed in combination with zeolite in different fields moving from pervaporation to water remediation (Rozek et al. 2019). Geopolymers also have large CO_2/N_2 selectivity in gas adsorption (Minelli et al., 2016; Minelli et al., 2019). For CO_2 capture, a geopolymer-zeolite 13X composite has been already investigated by thermogravimetric analysis, pressure decay tests (Minelli et al., 2018) and differential adsorption tests in CO_2/N_2 gas mixture flow (Boscherini et al., 2021), showing interesting capacity and selectivity.

In parallel, a numerical model has been developed to simulate both the continuous flow adsorption and the thermal effects associated with the process. The model can be employed to predict the behaviour of the sorbent in different operating conditions such as higher or lower temperature of the gas flow entering the bed and different CO_2/N_2 ratio. The model can also provide useful indications for analysing the effect of scale up on the internal profiles of temperature and concentration.

2. Experimental setup of dynamic adsorption tests

Dynamic experiments are carried out in a glass fixed bed column with (diameter 25.7 mm and height 200 mm) filled by sorbent granules (400-630 µm size). The sorbent is a composite of zeolite 13X and Na based geopolymer (Boscherini et al., 2021) having specific surface area of 221 m^2/g. The feed gas (CO_2 and N_2) is regulated by electronic mass flowmeters. An external electric coil allows the heating of the column, insulated with multiple layers of Teflon tape. The bed temperature is measured by a K-type thermocouple in the outlet section of the column, while outlet concentration of the gas is monitored by a multicomponent gas analyser (Testo 350). The setup allows both complete adsorption tests, in which the bed is brought to saturation, and cyclic tests, where the adsorption step was interrupted at the breakthrough point (CO_2 outlet concentration equal to 5 % that in the feed). Captured CO_2 is calculated from the outlet concentration profiled over time, by integrating the mass balances for N_2 and CO_2 between the inlet and the outlet of the column (neglecting any N_2 adsorption):

$$q_{CO_2} = \frac{\dot{n}_{in}}{m_s} \int_{t_0}^{t_0+t_{ads}} \left(y_{CO_2}^{in} - y_{CO_2}^{out} \frac{1-y_{CO_2}^{in}}{1-y_{CO_2}^{out}} \right) dt \tag{1}$$

in which $\dot{n}$ is the molar flowrate, $y_{CO_2}^{in}$ and $y_{CO_2}^{out}$ are respectively the CO_2 inlet and outlet molar fractions of the gas flow, m_s is the mass of the sorbent, and t_0 and t_{ads} are the initial time and the duration of the adsorption test, respectively. A more detailed discussion on preparation and characterization of sorbent material, sorption apparatus and sorption tests conditions, reference can be found in a previous work (Boscherini et al., 2021).

3. Model description

The 1-D (plug flow assumption) computational model employed for the simulations has been developed and implemented in FORTRAN, based on continuum thermomechanics, as well as mass and energy transport. The gas phase is described by the Peng-Robinson equation of state, while Sips equation represents CO_2 adsorption in the sorbent phases (using 7 parameters retrieved from best fit of experimental static adsorption isotherms at different temperatures, Foo and Hameed (2010)). The model accounts only for CO_2 adsorption and a linear driving force (LDF) approach is considered for adsorption kinetics (Gholami and Talaie, 2010). The model solves the differential equations of mass, species, energy and momentum in the domain ($0 \leq t$; $0 \leq z \leq L$), where L is reactor length, through a time implicit finite volume discretization method: a grid of 100 equally spaced nodes in the axial direction (z) and a constant time-step are used. The iteration for pressure, concentration and temperature profiles is conducted in three nested loops. The complete set of equations solved by the model is the following:

$$\begin{cases} \varepsilon_t \dfrac{\partial c}{\partial t} + \dfrac{\partial n}{\partial z} + \rho_b \dfrac{\partial q_{CO_2}}{\partial t} = 0 \\[2ex] \varepsilon_t \dfrac{\partial \left(c\, y_{CO_2} \right)}{\partial t} + \dfrac{\partial \left(n\, y_{CO_2} \right)}{\partial z} + \rho_b \dfrac{\partial q_{CO_2}}{\partial t} - \varepsilon_b \dfrac{\partial}{\partial z}\left(cD \dfrac{\partial y_{CO_2}}{\partial z} \right) = 0 \\[2ex] \dfrac{\partial q_{CO_2}}{\partial t} + k_s \left(q_{CO_2} - q_{CO_2}^* \right) = 0 \\[2ex] \left[\varepsilon_t \hat{C}_g c + \rho_b \left(\hat{C}_s + q_{CO_2} c_{CO_2}^{ads} \right) \right] \dfrac{\partial T}{\partial t} + n\hat{C}_g \dfrac{\partial T}{\partial t} - \rho_b \Delta \tilde{H}_{ads} \dfrac{\partial q_{CO_2}}{\partial t} - \varepsilon_b \dfrac{\partial}{\partial z}\left(k_g \dfrac{\partial T}{\partial z} \right) + \dfrac{2}{R_p} h\left(T - T_\infty \right) \\[2ex] \dfrac{\partial p}{\partial z} + \left[1.75n + \dfrac{150\mu\left(1 - \varepsilon_b \right)}{d_p} \right]\left(\dfrac{1 - \varepsilon_b}{\varepsilon_b^3\, d_p} \right)\dfrac{n}{c} = 0 \end{cases} \qquad (2)$$

In these equations, y_{CO_2} is the fraction of active component in the gas phase, n is the molar flux density of the gas in the axial direction and q_{CO_2} is the concentration of active component adsorbed in the solid (q^* is the corresponding CO_2 capacity), c is the gas phase concentration (Peng-Robinson). C_g is the gaseous phase heat capacity linearly dependent on temperature and composition, while μ is the (constant) viscosity of the gas phase and the axial dispersion coefficients for mass transfer (D) and heat transfer (k_g) are calculated as functions of sorbent particle diameter, total void fraction, molar flux density, gas concentration and molecular diffusivity. R_p is the radius of the column, while ε_t and ε_b are respectively its total and bed void fractions. The equations are integrated with the following boundary conditions:

$$\begin{cases} z = 0 \quad \Rightarrow \quad y_{CO_2} = y_{CO_2}^{(in)}(t); \quad T = T^{(in)}(t); \quad n = \dfrac{\dot{V}_{CO_2}^{in} + \dot{V}_{N_2}^{in}}{\pi\, r^2} \dfrac{p}{RT} \\[2ex] z = L \quad \Rightarrow \quad \dfrac{\partial y_{CO_2}}{\partial z} = \dfrac{\partial T}{\partial z} = 0; \quad p = p^{(out)}(t) \\[2ex] p^0 = p^{(out)}(t = 0) \end{cases} \qquad (3)$$

As for the initial conditions of the bed, the model is set to calculate the initial CO_2 content in the bed starting from the set regeneration conditions.

4. Experimental and model results

Figure 1 compares the experimental complete adsorption and desorption test, with the one obtained by the model, showing outlet CO_2 concentration profiles over time, with an inlet CO_2 content of 14.0 mol.%. The experimental test is carried out at room temperature of 23 °C with no external heating of the column, and the simulation uses this temperature both as initial bed temperature and room temperature, assuming equilibrium between column and environment at time 0 of the simulation; Use is made of Sips' equation parameters determined from static adsorption tests.

The experimental breakthrough time lasts 6.5 min, thanks to the good capacity of the sorbent, afterwards CO_2 concentration rises significantly. Noteworthy, the CO_2 concentration behaviour shows an evident knee as the sorbent material approaches saturation, after a certain time lag is observed, and the sharp increase at BT time; a similar behaviour is also visible in the desorption branch. Such behaviour could be explained by the recorded temperature profile, which presented an appreciable increase and a peak at about 36 °C corresponding to breakthrough time (Boscherini et al., 2021). Such thermal effects are the footprint of the exothermic nature of adsorption, and may lead to undesired effects on the whole process, lowering the resulting CO_2 capacity. The Sips equation, obtained from long time equilibrium adsorption tests, estimates a CO_2 capacity loss of about 25%, for the observed temperature rise of 13°C.

The numerical model has been first validated to describe the experimental results, and it has been found that it is suitable to represent both concentration and temperature profiles (Boscherini et al., 2021). As seen in figure 1, the model with optimized parameters provided a good fit of the experimental data both for concentration and temperature profiles. In this work, use is made of the model to asses, in a predictive fashion, the effect of process conditions and design on CO_2 capacity and efficiency of adsorption (defined as the ratio between the moles of CO_2 captured and total number of moles of CO_2 fed to the column) at breakthrough point, as well as breakthrough time and adsorption peak temperature. In particular, the effect of inlet feed temperature, external heat transfer coefficient and sorbent bed dimensions (aiming to scale up from lab to industrial scale) are

considered. The column has been scaled by a factor of 10 both in length and diameter, maintaining the ratio constant, starting from the lab scale column (25 mm ID and 197 mm length), as well as the same frontal velocity of the gas. Therefore, the feed flow rate in the lab scale column is 0.0454 kg/h, while 4.54 kg/h in the scaled-up configuration. The comparison among the two configurations has been carried out at two different feed CO_2 concentration, namely 20 and 10 mol.%.
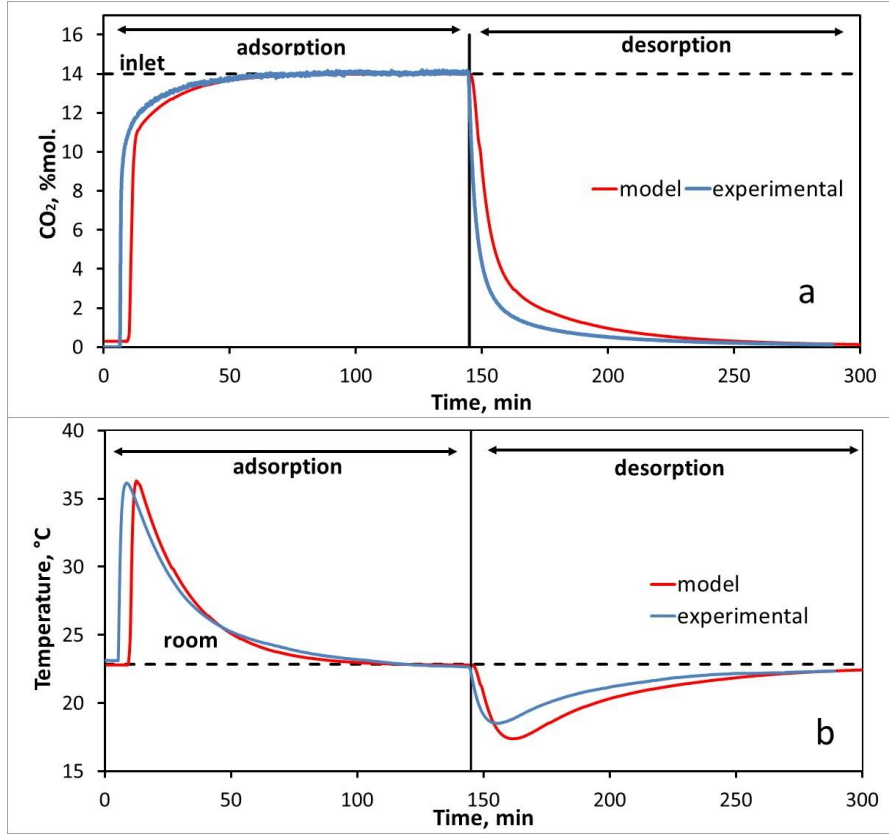

Figure 1: Comparison of modelled (red) and experimental (blue) breakthrough profiles over time for an inlet CO_2 concentration (dashed black line) set at 14 mol.%. Vertical black line at 143 min indicates the switch between adsorption and desorption. To best fit the experimental data, the model assumes an initial CO_2 fugacity in the bed of 3 mbar and an external heat transfer coefficient of 9 $W/(m^2 K)$ (Boscherini et al., 2021)

Table 1 summarizes the results obtained from the numerical simulations, and reported in terms of BT time, captured CO_2 and resulting peak temperature. Furthermore, the resulting data allows the determination of the adsorption efficiency (mol CO_2 fed/mol CO_2 captured) and the effects of inlet temperature, scale up and external heat exchange coefficient on the capture performance.

Table 1: CO_2 capture performances of the sorbent bed calculated by numerical simulation in various cases.

	feed (kg/h)	$y_{CO_2}^{in}$	T_{in} (K)	U (W/m² K)	t_{BT} (min)	T_{peak} (°C)	CO_2 captured (at BT) (mol)	adsorption efficiency
lab scale	0.0454	0.2	298	10	10.9	39.5	0.0527	0.9923
scale up	4.54	0.2	298	10	113	41.5	54.7	1.0000
lower T_{in}	0.0454	0.2	273	10	11.6	38.4	0.0561	0.9978
high T_{in}	0.0454	0.2	323	10	10.9	40.2	0.0531	0.9999
higher T_{in}	0.0454	0.2	573	10	9.67	50.2	0.0463	0.9885
larger U	0.0454	0.2	298	15	11.6	37.8	0.0562	0.9998
lower U	0.0454	0.2	298	5	11.6	39.0	0.0558	0.9929
10% feed (lab scale)	0.0454	0.1	298	10	18.0	37.7	0.0443	0.9609
10% feed (scale up)	4.54	0.1	298	10	163	40.5	41.7	1.0000

The adsorption efficiency is remarkably high (above 0.96) in all simulated conditions, and near 1.0 in most cases. Clearly, before breakthrough CO_2 capture is very efficient because the sorbent is not exhausted, Furthermore, inlet temperature and heat exchange coefficient have a moderate effect on captured CO_2 and peak temperature, and only a 300 °C feed temperature produces appreciable changes with respect to the base case considered (feed room temperature). Conversely, the breakthrough time depends on the size of the sorbent bed, and a factor 10 is observed as expected, from the lab scale to the larger size bed, accompanied by an increase of the capture efficiency, evident both for 10 and 20% of CO_2 feed concentration.

Figure 2 illustrates in detail the comparison between small (lab-scale) and large (scaled-up) sorbent bed in terms of CO_2 profiles in the gas phase in the sorbent bed (in the void space between the granules) along the dimensionless axial coordinate (z position/length) and internal temperature at different dimensionless times (i.e. rescaled by characteristic time of the reactor, calculated as the travel time of the gas in the reactor, from reactor length and gas frontal velocity) for 10 mol. % of the CO_2 feed concentration. The concentration in the whole sorbent bed would be near zero at early times, as all the CO_2 fed is adsorbed the geopolymer-zeolite composite granules (the feed is at z/L=0 and the sorbent bed is located between 0.08 and 0.95, considering thus upstream and downstream dead zones, as in real application). Shortly after the breakthrough, an increasing portion of the bed (feed is from the left side of the plot) reaches saturation conditions and CO_2 is also present in the gas phase. Temperature profiles clearly point out the exothermic nature of the process, as indicated by the temperature increase of about 15°C for all cases that involves larger portions of the sorbent bed as the time proceeds.
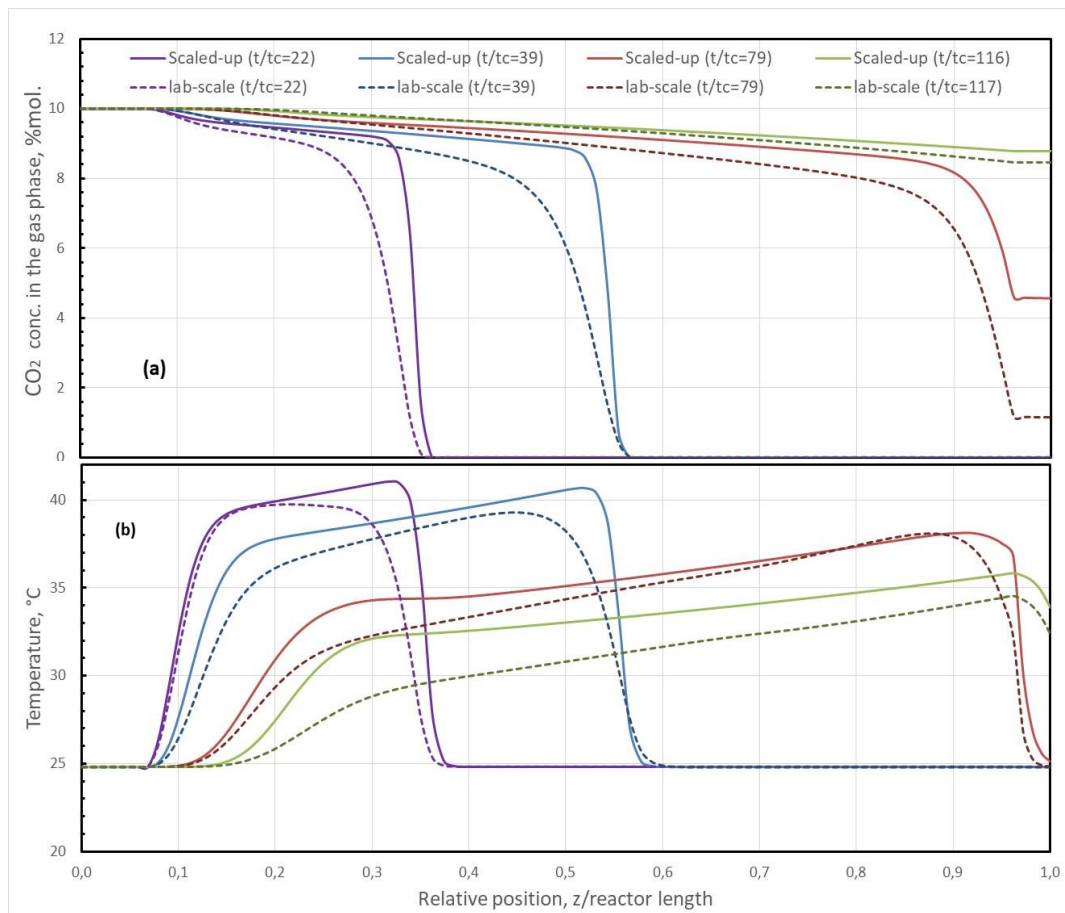

Figure 2: Simulated adsorption profiles in the sorbent bed of (a) CO_2 gas concentration; and (b) temperature (b), plotted as function of dimensionless axial coordinate and dimensionless time (10% CO_2 feed concentration): comparison between lab-scale (dashed lines) and scaled-up (continuous line) sorbent bed.

The plots show qualitatively similar behaviours for the two cases inspected, and both T and y_{CO2} profiles are comparable at the same dimensionless times. However, it is noteworthy that the CO_2 concentration profiles in the scaled-up sorbent bed is appreciably sharper than those in the lab-scale system, indicating a more efficient exploitation of the adsorption process, as one can see also in the capture efficiency reported in Table 1. The characteristic times, even rescaled with the different t_c for lab-scale and scaled up, result slightly larger in the

latter one, and BT times are thus larger. The smoother temperature profiles for the lab-scale sorbent bed are also associated to the more effective heat exchange with the environment, due to the smaller size of the system.

5. Conclusions

The CO_2 adsorption/desorption process on the geopolymer- zeolite 13X composite and its associated thermal effects have been more deeply investigated by means of 1D numerical model purposely developed that was positively validated describing the experimental results previously obtained. The model is based on the Sips equation for the representation of CO_2 adsorption capacity, a thermodynamic approach for the gaseous phase and explicitly accounts for mass and energy transport in the sorbent bed.

The model could be then profitably exploited for the investigation of the adsorption/desorption behavior at different feed concentration, heat transport coefficient as well as inlet temperature. The results have been analyzed in terms of breakthrough time and peak temperature, as well as capture efficiency, revealing the relevance of the temperature profile in the sorbent bed, while pointing out that the most important contribution is represented by the heat of adsorption.

The model was also employed to compare the results obtained for a small size (lab-scale) adsorption bed with a scaled-up, industrial size, system. The analysis of the concentration and temperature profiles in the sorbent bed at different adsorption times allowed the comparison among the two different scales of the sorbent bed. Interestingly, moving from lab-scale to scaled-up system, the breakthrough time rises from 18 to 163 min and the peak temperature slightly increases from 38 to 41 °C.

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