DFT-based adsorption isotherms for pure and flue gas mixtures including SO$_2$ poisoning on Mg-MOF-74

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(graphical abstract)
ABSTRACT

A simplified model is applied for the prediction of gas/solid adsorption isotherms of pure gases (i.e., CO$_2$, N$_2$, SO$_2$) on the metal-organic framework Mg-MOF-74, based on periodic Density Functional Theory (DFT) calculations and a dual-site Langmuir approach (DFT/DSL), using a mean-field approximation for the inclusion of the lateral interactions. This model not only provides reliable adsorption isotherms ($P \leq 1$ atm, $293 \leq T \leq 373$ K) but also isosteric heats of adsorption in good agreement with both available experimental data and previous more refined models. Moreover, an extension of this model is used to study the effect of SO$_2$ as an impurity in the efficiency of adsorption and desorption processes of some post-combustion gas mixtures. It is shown that a very low concentration of SO$_2$ is enough to poison Mg-MOF-74 structure. Moreover, different swing adsorption techniques at different working conditions are analysed to reduce the impact of SO$_2$ poisoning in CO$_2$ separation.

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1. INTRODUCTION

Over the past decades, many efforts have been addressed for Carbon Capture, Utilization and Storage (CCUS) technologies on flue gas streams.$^{1,2}$ Several post-combustion CO$_2$ capture technologies including absorption, adsorption, cryogenics, membranes and so forth, have been studied.$^3$ Nowadays, most separation technologies involve solvents (e.g., amines), which demand high energy and result in potential unwanted environmental and economic consequences due to solvent loss and degradation.$^4$

Alternative technologies aimed to mitigate some of the disadvantages of these amine solutions have become an active area of research. Among them, solid absorbent materials have demonstrated potential capability in reducing costs and improving CCUS performance compared to existing systems.$^5,6$ Finding the most efficient absorbents has attracted a lot of both experimental and theoretical research, and even a wide variety of new absorbents have been proposed and synthesized for using in post-combustion CO$_2$ capture.$^7,8,9,10,11,12,13$

Metal–Organic Frameworks (MOFs) have received significant attention. They are porous structures, with high thermal stability,$^{14}$ adjustable chemical functionality,$^{15}$ extra-
and hundreds of crystalline well-characterized porous structures are available.\textsuperscript{17,18,19,20,21} In fact, some of them have demonstrated high CO\textsubscript{2} adsorption capacities and high selectivities for CO\textsubscript{2} over N\textsubscript{2}, in addition to reduced regeneration energy penalties.\textsuperscript{5,22,23,24,25} One of the most interesting MOF for CO\textsubscript{2} capture is Mg-MOF-74 (also known as CPO-27-Mg or Mg\textsubscript{2}(DOBDC)).\textsuperscript{26} This MOF is based on helical chains of Mg\textsuperscript{2+} located at the intersections of honeycomb-like structures formed by 2,5-dioxido-1,4-benzenedicarboxylate (DOBDC\textsuperscript{4−})\textsuperscript{27} linkers with large one-dimensional pores of approximately 12 Å diameter. Mg\textsuperscript{2+} atoms present an octahedral coordination with oxygen atoms of linkers. Each Mg\textsuperscript{2+} ion in the evacuated structure bears an open-metal site, which is a highly favourable adsorption site for various guest molecules. Currently, Mg-MOF-74 displays one of the best adsorption performances for many gas molecules, with CO\textsubscript{2} uptakes as high as 8.08 mol·kg\textsuperscript{−1} at 298 K and 1.0 atm, associated with a high initial isosteric heat of adsorption value (i.e., 47 kJ/mol at low surface coverages).\textsuperscript{27} The unsaturated sites are the cause of strong interactions with CO\textsubscript{2} molecules due to its large quadrupole moment and polarizability.\textsuperscript{28}

Nevertheless, in general, it has been shown that the presence of gas impurities in the flue gas mixture affects the efficiency of carbon dioxide capture processes.\textsuperscript{29,30,31} Although there are noticeable studies on adsorption of CO\textsubscript{2} and some other gases on Mg-MOF-74, limited studies have concerned the effect of impurities such as SO\textsubscript{2} and NO\textsubscript{x} on the CO\textsubscript{2} capture process on MOFs.\textsuperscript{32,33,34,35}

In this regard, molecular simulation methods, such as Grand Canonical Monte Carlo and Molecular Dynamics have made an important contribution to the understanding of gas adsorption and separation in porous materials.\textsuperscript{36} In general, these studies use suitable force fields for predicting the intermolecular solid/fluid and fluid/fluid interactions, which are less expensive than quantum-chemical calculations for the evaluation of energies and forces.

Recent theoretical studies on Mg-MOF-74\textsuperscript{40,41} revealed that the correct description of gas/MOF dispersion corrected DFT adsorption energies, partition functions and gas/gas lateral interactions, which can be used to obtain thermodynamic functions at different coverages (i.e., $\Delta U(\theta)_{ads}$, $\Delta H(\theta)_{ads}$, $\Delta S(\theta)_{ads}$ and $\Delta G(\theta)_{ads}$), can be combined in a multi-site Langmuir model to predict adsorption isotherms at any temperature and pressure. These electronic structure calculations are able to reproduce the gas/metal interactions accurately, that will be the main driving force of adsorption at
low pressures, and also the gas/gas interactions, which can have an important effect in the adsorption properties of Mg-MOF-74 at high pressures. Additionally, the reliable gas/MOF interactions described by DFT ensures the correct evaluation of poisoning effects at low concentration of pollutants (i.e., < 1 mol %), which is controlled by the competition for MOF sites between the pollutants and other gas molecules.

Among the works previously published, Sillar et al. recently studied the adsorption of CO₂ in Mg-MOF-74 using a dual-site Langmuir model enhanced with gas/gas lateral interactions. Their adsorption energies and other thermodynamic functions were calculated using a combination of periodic and high accuracy cluster models; for more information, the reader is referred to the original paper. 40 Also, they obtained the lateral interactions with the calculation of each pair of interacting molecules explicitly and then, the coverage dependent lateral interactions were averaged to be treated as a mean-field. The present work intends to simplify the model of Sillar et al. by using only periodic DFT calculations instead of a combination of periodic and cluster models, and also reducing the number of calculations needed to build a reasonable adsorption isotherm to only four adsorption processes, which is possible by simplifying the model of the gas/gas lateral interactions. With the previous simplifications in the model of Sillar et al., pure adsorption isotherms and the coverage dependent differential isosteric heats were predicted for CO₂, N₂ and SO₂ in good comparison with both the previous theoretical and experimental results when available. Furthermore, combination of DFT calculations with dual-site Langmuir model (DFT/DSL) was extended to treat ternary mixtures of CO₂, N₂ and SO₂ with the aim of quantifying the SO₂ poisoning impact on a model flue gas stream.
2. METHODS AND COMPUTATIONAL DETAILS

2.1 Density Functional Theory Calculations. The adsorption of gas molecules onto Mg-MOF-74 was first studied by means of periodic DFT calculations performed with Vienna ab-initio Simulation Package (VASP).\textsuperscript{42,43} The dispersion corrected VDW-DF2 functional\textsuperscript{44,45} was selected because it accurately reproduces gas/MOF interactions, especially the CO\textsubscript{2}/MOF binding energies accounting also for van der Waals interactions.\textsuperscript{46} The projected augmented wave potential\textsuperscript{47} (PAW) technique was used for the core electrons, while valence electrons were treated explicitly with a plane wave expansion with a kinetic energy cut-off of 600 eV. All calculations were carried out with a reciprocal cell containing only the Γ point due to the large size of the real simulation cell, and interaction energies and forces were converged up to 10\textsuperscript{−6} eV and 10\textsuperscript{−4} eV/Å, respectively.

The simulation cell used is the rhombohedral structure presented in Figure 1, which contains 12 Mg\textsuperscript{2+} sites and 12 (DOBDC\textsuperscript{4−}) Linker sites per pore, and it is large enough in all directions to prevent the interactions of the adsorbed gas molecules with their periodic images. Gas/MOF adsorption energies (\(\Delta E_{\text{ads}}\)) were calculated according to eq 1, first minimizing the full MOF structure at VDW-DF2 level, and then relaxing the gas molecule on the surface along with the nearest MOF atoms (i.e., those surface atoms closer than 7 Å to any atom of the gas molecule). All minima were characterized with frequency calculations that were used to obtain the corresponding partition functions\textsuperscript{48} necessary to calculate the adsorption thermodynamic functions \(\Delta H_{\text{ads}}\) and \(\Delta S_{\text{ads}}\), which can be related to \(\Delta G_{\text{ads}}\) through eq 2. In our model, translational, rotational and vibrational partition functions were calculated for the gas molecules, but 3N normal modes were considered as harmonic vibrations after adsorption (i.e., all pure vibrational modes along with the frustrated rotations and translations). The translations, rotations and vibrations of the substrate were neglected because they remained almost constant upon gas adsorption, and its contribution vanished when \(\Delta G_{\text{ads}}\) was calculated. To ensure the validity of this approximation, the adsorption of one CO\textsubscript{2} molecule onto a Mg\textsuperscript{2+} site at 298 K was calculated considering the vibrations of the 61 nearest MOF atoms resulting in a negligible difference in the final \(\Delta G_{\text{ads}}\) value (i.e., 1.05 kJ/mol). For more detailed
information on the present calculation of all thermodynamic functions obtained from DFT data the reader is referred to Sect. S1 of the Supporting Information).

\[ \Delta E_{ads} = E_{MOF/gas} - E_{MOF} - E_{gas} \] (1)

\[ \Delta G_{ads} = \Delta H_{ads} - T\Delta S_{ads} \] (2)

### 2.2 Obtaining Isotherms from a DFT-based Dual-Site Langmuir Adsorption Model

To predict the adsorption isotherm of a pure gas onto a surface, the single-site Langmuir isotherm model cannot be successfully used due to the assumptions made by Langmuir in its derivation 49: i) all sites are equivalent, ii) there are no interactions between molecules, and iii) each site can hold at most one molecule. The first assumption does not apply in our case because Mg-MOF-74 presents two main different adsorption sites.26 The second assumption neglects adsorbate lateral interactions, which may have important effects as shown in the discussion of this work and by other authors.40,41,50

Finally, the third statement in principle will be true at low pressures for small gas species according to previous experimental and theoretical adsorption studies on MOFs.35,46,51,52

For these reasons, two different adsorption sites are accounted for by using a dual-site Langmuir isotherm model (eq 3),53 which assumes that the coverage at each adsorption site is governed by a single Langmuir isotherm with its own equilibrium constant. With this assumption, the total coverage (\( \theta \)) can be obtained by the sum of two individual Langmuir isotherms, the first regarding the coverage of Mg\(^{2+} \) sites (\( \theta_{Mg^{2+}} \)) and the second accounting for the coverage at the Linker sites (\( \theta_L \)), multiplied by the site distribution \( \chi_i = N_i/N_{tot} \), with \( i = Mg^{2+} \) or \( L \), and \( N_{tot} \) the total number of sites. In Mg-MOF-74 the number of Mg\(^{2+} \) and Linker sites is the same, which implies that \( \chi_{Mg^{2+}} = \chi_L = 0.5 \). On the other hand, the gas-gas lateral interactions will modify the adsorption Gibbs free energy with the surface coverage, which makes the equilibrium constant to be also dependent on this magnitude (eq 4) 53,

\[ \theta = \chi_{Mg^{2+}} \theta_{Mg^{2+}} + \chi_L \theta_L = \chi_{Mg^{2+}} \frac{K_{Mg^{2+}}(\theta) P}{1 + K_{Mg^{2+}}(\theta) P} + \chi_L \frac{K_L(\theta) P}{1 + K_L(\theta) P} \] (3)

\[ K_i(\theta) = \frac{1}{P_o} e^{-\Delta G_{ads}(\theta)/RT} \] (4)
being \( P_0 \) the standard pressure (i.e., 1 atm).

With eqs 3-4 one can obtain the adsorption isotherm of a pure gas species adsorbed on the Mg-MOF-74 surface from \( \Delta G_{i,ads}(\theta) \) for both Mg\(^{2+}\) and Linker sites, which formally depends on the temperature and the surface coverage of both sites. In this work, we simplified the calculation of lateral interactions assuming that \( \theta_L \) is small according to previous theoretical and experimental adsorption studies with many gases at the selected pressures of the present work\(^{26,51,54}\). This assumption implies that \( \Delta G_{i,ads}(\theta) \) in our model will only depend on the temperature, the nature of the adsorption site \( (i) \) and the coverage on Mg\(^{2+}\) sites \( (\theta_{Mg^{2+}}) \). A mean-field (MF) approximation is used \(^{55,56}\) to evaluate the coverage dependence in \( \Delta G_{i,ads}(\theta) \), which is considered a linear function between \( \Delta G_{i,ads}(\theta \approx 0) \), when adsorbing a gas molecule in the empty framework, and \( \Delta G_{i,ads} \), when adsorbing a molecule in a Mg\(^{2+}\) fully loaded structure, both values calculated with eq 2. Within this approximation \( \Delta(\Delta G_{i,ads}) \) is defined as the difference between the Mg\(^{2+}\) full-coverage and the zero-coverage values, being the final coverage dependent Gibbs free energy defined by eq 5.

\[
\Delta G_{i,ads}(\theta) = \Delta G_{i,ads}(\theta \approx 0) + \theta_{Mg^{2+}} \cdot \Delta(\Delta G_{i,ads})
\]  

In order to obtain the coverage at equilibrium at a given pressure \( (P) \) and temperature \( (T) \) using \( \Delta G_{i,ads} \) DFT values, eq 3-5 must be solved iteratively by using \( \Delta G_{i,ads}(\theta \approx 0) \) quantity as initial value in the first iteration and replacing the result of \( \theta_{Mg^{2+}} \) obtained from eq 3 into eq 5 until the convergence of the total coverage \( (\theta) \) is achieved. Although this method allows obtaining adsorption isotherms by only characterizing the adsorption sites and its lateral interactions, the final adsorption isotherms obtained by this method will be reliable at moderate pressures and temperatures. Also, the mean-field approximation considers the effect of co-adsorption as an average field, instead of a local effect. This implies that molecular arrangements such as islands cannot be observed with this method. However, the present work demonstrates that even with these limitations, this DFT/DSL model can successfully predict adsorption isotherms and isosteric heats of adsorption with a high degree of accuracy.
2.3 Prediction of the Isosteric Heat Dependence with Coverage in Mg-MOF-74.

The adsorption enthalpy (integral value) can be obtained by summing the enthalpy of adsorption contributions of both sites (eq 6),

\[
\Delta H_{\text{ads}}(\theta) = \theta_{Mg^{2+}} \cdot \Delta H_{Mg^{2+},\text{ads}}(\theta) + \theta_L \cdot \Delta H_{L,\text{ads}}(\theta)
\]

(6)

where each enthalpy depends on the temperature, the nature of the adsorption site and the surface coverage, so mean-field approximation is also applied to determine the value of \( \Delta H_{L,\text{ads}}(\theta) \) with an expression analogous to eq 5 but using enthalpies instead of Gibbs free energies.

The isosteric heat of adsorption \( (q_{st}) \) can be obtained from the partial derivative of \( \Delta H_{\text{ads}}(\theta) \) with respect to the coverage at constant temperature (eq 7).

\[
q_{st} = - \left( \frac{\partial \Delta H_{\text{ads}}}{\partial \theta} \right)_T
\]

(7)

Alternatively, \( q_{st} \) was also calculated using the Clausius-Clapeyron equation, which arises from the slope of the ln(P) vs. 1/T isostere (eq 8). This methodology is extensively used in experimental studies and requires the measurement or calculation of isotherms at different temperatures to build the isostere, assuming that \( \Delta H_{\text{ads}} \) is approximately constant in the working range of temperatures. Both methods were used and compared to obtain \( q_{st} \) at several coverages and temperatures, showing equivalent results.

\[
\left( \frac{\partial \ln(P)}{\partial (\frac{1}{T})} \right)_\theta = \frac{q_{st}}{R}
\]

(8)

3. RESULTS AND DISCUSSION

3.1 Analysis of the Main Adsorption Sites: DFT Adsorption Energies, Enthalpies, Entropies and Gibbs Free Energies. The adsorption of single CO\(_2\), N\(_2\) and SO\(_2\) molecules onto the two main adsorption sites (taken here as approximately zero-
coverage) was analysed at DFT level, showing in all cases that Mg$^{2+}$ is the most favourable site when compared to the Linker. These sites are shown in Figure 2 with CO$_2$ molecules adsorbed on them. The adsorption energies obtained (including ZPE) onto the Mg$^{2+}$ sites were -46.1 kJ/mol, -29.3 kJ/mol and -78.9 kJ/mol for CO$_2$, N$_2$ and SO$_2$, respectively, in good agreement with the theoretical results available in the bibliography (i.e., -41.0/-44.9 kJ/mol for CO$_2$, $^{60,61,62,63}$ -28.0/-28.5 kJ/mol for N$_2$ $^{62,63}$ and -62.0/-88.0 kJ/mol for SO$_2$ $^{62,63,64}$). Also, these results show a much stronger adsorption for SO$_2$ than for CO$_2$ according to the poisonous nature of SO$_2$ $^{29}$. In contrast, the adsorption on the Linker sites presents a binding energy of -29.5 kJ/mol for CO$_2$ and -36.6 kJ/mol for SO$_2$, while no adsorption is observed for N$_2$. Unfortunately, to our knowledge, there are no data reported on the adsorption properties of the Linker for these molecules, but our results show that CO$_2$ and SO$_2$ molecules present weak adsorption on these sites.

Statistical thermodynamics is applied to obtain the enthalpy, entropy and Gibbs free energy of adsorption for the three molecules on the available sites at 298 K, which are listed in Table 1. The analysis shows that the adsorptions of both CO$_2$ and SO$_2$ on the Mg$^{2+}$ sites are spontaneous processes, whereas their adsorptions onto the Linker sites are not. Alternatively, N$_2$ does not present any spontaneous adsorption process onto Mg-MOF-74, neither on the Mg$^{2+}$ sites or the Linker sites at 298 K, which explains its low affinity for this adsorbate.

Despite our calculations used to obtain the thermodynamic functions involved a single optimization in a DFT periodic model, which is a simplification of the periodic (DFT) + cluster (MP2/CCSD(T)) method used by Sillar et. al. $^{40}$, our results for the enthalpy and Gibbs free energy of adsorption are in good agreement within the chemical accuracy of 4 kJ/mol at both 298 K and 343 K. This agreement can be seen in Table 2 and validates the simplification of the methodology used to obtain the thermodynamic functions by using only periodic DFT calculations.

The $\Delta G_{\text{ads}}$ dependence with the gas molecules adsorbed either on the Mg$^{2+}$ sites or on the Linker sites with the Mg$^{2+}$ coverage at several temperatures was also studied, as detailed in Sect. S2 of the Supporting Information. Thermodynamic functions at $\theta_{\text{Mg}^{2+}} = 1$ and 298 K are reported in parentheses in Table 1. In general, the Mg$^{2+}$ coverage has a strong effect on the adsorption properties of the Linker sites due to the proximity of these two kinds of sites (i.e., approximately 3.7 Å). On the other hand, the Mg$^{2+}$ coverage have a weaker effect on the Mg$^{2+}$ adsorption properties because the distance between two Mg$^{2+}$
sites is approximately 7 Å. Concretely, the adsorption on the Linker site is enhanced by the Mg$^{2+}$ coverage, which means that the binding energies and all thermodynamic functions of gas molecules adsorbed on these sites become more negative, also increasing the equilibrium constants of these sites by some orders of magnitude. Finally, notice that when all Mg$^{2+}$ sites are occupied, the Linker/N$_2$ adsorption site appears as a minimum with a very low equilibrium constant.

3.2 DFT-Based Pure Gas Adsorption Isotherms. DFT/DSL isotherms for pure CO$_2$, N$_2$ and SO$_2$ on Mg-MOF-74 were calculated up to a pressure of 1 atm. The isotherms were built solving eq 3-5 for each pressure at 298 K to compare with previous reported results in the bibliography when available.$^{26,35,65,66}$ Note that all experimental adsorption isotherms are measured as excess quantities, whereas our calculations yield the absolute adsorbed amounts. However, this difference is negligible for relatively low pressures (e.g., for CO$_2$ on Mg-MOF-74 with $P \leq 5$ atm$^{40}$).

It is worth noting that DFT/DSL model gives an upper value of the total adsorption on Mg-MOF-74 due to the assumption that the crystal has all its sites available for adsorption. However, experimentally some sites might be blocked with poisonous species adsorbed during the synthesis, or even defects in the MOF structure that can affect the adsorption site distribution as noted by other authors$^{40,41,50}$. Specifically, depending on the procedure employed for the synthesis of the MOF structure it may yield different adsorption availabilities as proven by Wu et al.$^{65}$ For this reason, results from the bibliography for CO$_2$ adsorption onto Mg-MOF-74 were analysed to derive an average MOF availability to include a scaling factor onto our isotherms, which accounts for this lack of site availability. The scaling factor was validated according to the experimental data of Dietzel et al.,$^{66}$ whose results are in very close agreement with the isotherms measured by Mason et al.,$^{26}$. On the other hand, Wu et al., used two different procedures to synthesize the Mg-MOF-74. The first procedure yielded adsorption isotherms in good agreement with Dietzel and Mason (data set 1), however, the second procedure produced a highly functional Mg-MOF-74 structure, with a substantially higher total uptake (data set 2). Also, Queen et al.,$^{51}$ obtained adsorption isotherms in between of the two previous data sets (data set 3). The scaling factor was obtained rescaling our DFT/DSL adsorption isotherms to match the uptake of 8.24 mol/kg of the experimental isotherms, which corresponds to a $\theta = 0.5$ and $\theta_{Mg^{2+}} \approx 1$. Scaling factors were obtained for the three
different experimental data sets at different temperatures when available. Data set 1 showed an average availability of 78.5 % at 293 K, whereas it presented an availability of 83.5% at 343 K. The average availability of this data set is 81.0 %, which is in good agreement with the values derived by Sillar et al., (76.5 %-78.0 %) in their previous works.\textsuperscript{40,41,50} Mason performed a fitting of the experimental CO\textsubscript{2} isotherms onto Mg-MOF-74 from 0 to 50 atm with a dual-site Langmuir model, obtaining a Mg\textsuperscript{2+} site saturation parameter of 6.8 mol/kg. For a perfect crystal, the Mg\textsuperscript{2+} site availability is exactly one CO\textsubscript{2} molecule per Mg\textsuperscript{2+} site, which corresponds to 8.24 mol/kg, so the experimental availability calculated by Mason et al. is 82 %, which is also in good agreement with the availability value proposed. In contrast, data set 2 reported only by Wu et al., presented an availability of 93.0 % at a temperature of 298 K. Finally, a site availability of 86.5 % at 298 K was derived from data set 3 of Queen et al., which is slightly above data set 1. Since the majority of results reported in the bibliography have an availability approximately of 81.0 %, only two DFT/DLS isotherms per gas molecule were plot in Figure 3: the perfect crystal isotherm (red lines) and the rescaled isotherm assuming 81 %-availability (blue lines). Two experimental data sets are also shown in Figure 3 for comparison, where our perfect crystal DFT/DLS isotherm lies slightly over the data set 2 from Wu et al., and the 81%-availability isotherm is in good agreement with the data set 1 from Dietzel, Mason and Wu. The results from Queen et al. were not shown for cleanliness.

It should also be noted that the DFT/DLS isotherm is still in good agreement with the experimental uptake of CO\textsubscript{2} at a pressure of 1 atm. This fact confirms the validity of the assumption made in the model neglecting the variation of thermodynamic functions with the Linker coverage. Regarding N\textsubscript{2}, DFT/DLS isotherm also accurately reproduces the experimental results from Mason et al.,\textsuperscript{26} and Wu et al.,\textsuperscript{65} at 298 K. Finally, to our knowledge, reliable experimental results for adsorption isotherms on Mg-MOF-74 are not available in the literature for SO\textsubscript{2}.

Our results seem to suggest that the open metal sites are subject to a higher level of poisoning by SO\textsubscript{2}, potentially displacing all CO\textsubscript{2} in a hypothetical mixture, which is also deduced from the difference in adsorption energies between these gases (i.e., -46.1 kJ/mol for CO\textsubscript{2} and -78.9 kJ/mol for SO\textsubscript{2}, in Table 1). The large SO\textsubscript{2} uptake at low pressures implies that this gas is capable of poisoning Mg-MOF-74, outcompeting CO\textsubscript{2} even in very
low concentrations (e.g., 1,000 ppm). Similar conclusions were also achieved by other studies already published in the literature.\textsuperscript{35,63}

DFT/DSL can also provide adsorption isotherms at different temperatures only by changing the temperature in equations of Sect. 2 without requiring further calculations. With this practice, the 81%-availability DFT/DSL isotherms for CO\textsubscript{2} and N\textsubscript{2} were compared with the reliable and extensive experimental data from Mason et al.,\textsuperscript{26} for temperatures ranging from 293 K to 373 K (see Figure 4). The $\Delta G_{i,ads}$ at different temperatures necessary for building isotherms are reported in Sect. S2 of the Supporting Information. 81%-availability SO\textsubscript{2} isotherm was also obtained, but no reliable experimental data was available to compare with our theoretical results. In general, all isotherms reduce their uptakes with the increase of temperature, but always in a reasonable agreement with reported isotherms. However, instead of using the harmonic approximation for all normal modes in the calculation of adsorbed CO\textsubscript{2} partition functions, some authors considered that the lowest frequency should be accounted as a 1D free rotation to avoid overestimating the entropy loss upon adsorption.\textsuperscript{40} This consideration applies at higher temperatures, where adsorbed molecules have enough thermal energy to overcome the rotational barrier of the weakest frustrated rotational mode. The use of a 1D free rotational partition function generally makes the value of $\Delta G_{i,ads}$ more negative, enhancing the gas/adsorbate interactions. In the present work, only the harmonic approximation was considered for simplicity, so it is expected that adsorption isotherms could be somewhat underestimated at very high temperatures because the 1D free rotational mode was not considered.

\textbf{3.3 Isosteric Heat of Adsorption Analysis.} The variation of $q_{st}$ with coverage for each gas at 298 K is shown in Figure 5, calculated by using eq 7 from a single isotherm (also coincident with Clausius-Clapeyron equation using isotherms from 293 K to 313 K to build the isostere). In general, the plot in Figure 5 shows three different regions: i) a low coverage region (i.e., from $\theta = 0$ to $\theta = 0.3$), where $q_{st}$ is almost constant (for instance, $-\Delta H_{Mg,ads} = 44.7$ kJ/mol for CO\textsubscript{2} at zero-coverage, except for the case of SO\textsubscript{2} that depicts a growing trend due to the increase of $-\Delta H_{Mg,ads}$ with the coverage), ii) a high coverage region (i.e., from $\theta = 0.7$ to $\theta = 1$), where $q_{st}$ is constant (e.g., $-\Delta H_{k,ads} = 32.1$ kJ/mol for CO\textsubscript{2} at full Mg\textsuperscript{2+} coverage, because the Mg\textsuperscript{2+} sites are
completely occupied and they stop contributing to the final isosteric heat; iii) an intermediate coverage region (i.e., from $\theta = 0.3$ to $\theta = 0.7$), where the Mg$^{2+}$ sites are close to saturation and the probability of a gas molecule to adsorb onto a Linker site becomes important. This implies that $q_{st}$ gradually decreases from the $-\Delta H_{Mg,ads}$ value onto the $-\Delta H_{L,ads}$ value, until the Mg$^{2+}$ sites are completely saturated. Also, this last region presents an inflection point when the Linker sites become the preferential adsorption site due to the lack of Mg$^{2+}$ ones, which can be also used as a measure of experimental availability.\textsuperscript{51,66}

The results obtained by DFT/DSL model reproduce the experimental $q_{st}$ values for CO\textsubscript{2} at different coverages, including the sigmoidal shape presented by the experimental data of Dietzel et al.\textsuperscript{66} and Queen et al.\textsuperscript{51} (Figure 5). This inflection point depends on the site availability, showing a clear shift to higher coverages as site availability increases. On the other hand, N\textsubscript{2} presents a low uptake at low and moderate pressures, and for this reason we only have derived the experimental zero-coverage $q_{st}$ of N\textsubscript{2} by using the Clausius-Clapeyron equation (eq 8) with the experimental data of Mason et al.\textsuperscript{26}, building the isostere with three isotherms at 293 K, 303 K and 313 K. With the available experimental pressure range, $q_{st}$ could only be determined up to $\theta = 0.1$, so only the zero-coverage value was determined (i.e., 22.5/23.5 kJ/mol), in good agreement with the DFT/DSL predicted result. Finally, no experimental data were available for SO\textsubscript{2} but according to our prediction it should present a very high initial $q_{st}$ almost doubling the $q_{st}$ of CO\textsubscript{2} at low coverages.

The present analysis reveals that SO\textsubscript{2} will have the highest affinity for Mg-MOF-74 at any coverage, saturating the Mg$^{2+}$ sites with a very high $q_{st}$ (i.e., from 77.5 to 86.5 kJ/mol) in contrast with CO\textsubscript{2} (i.e., from 44.7 to 42.5 kJ/mol) and N\textsubscript{2} (i.e., from 28.1 to 27.0 kJ/mol), which means that in hypothetical mixtures one should expect that SO\textsubscript{2} will easily poison Mg-MOF-74. After complete saturation of Mg$^{2+}$ sites, the linker sites show again the same trend in $q_{st}$ but with lower absolute values (i.e., 52.8 kJ for SO\textsubscript{2}, 32.1 kJ/mol for CO\textsubscript{2} and 12.7 kJ/mol for N\textsubscript{2}) the difference between $q_{st}$ for SO\textsubscript{2} and CO\textsubscript{2} is lower in the Linker sites than in Mg$^{2+}$ sites, so although the Linker will also suffer from poisoning, the effect is expected to be lower.
3.4. Impurity Effects and Henry’s constants. The adsorption isotherms shown in the previous sections along with the values of the isosteric heats of adsorption demonstrate the great affinity of Mg-MOF-74 for SO₂, according to the ranking SO₂ > CO₂ > N₂. However, in mixtures where low partial pressures of impurities (e.g., SO₂) are present, the main parameter that gives information about the rate of poisoning with pollutants is the ratio between the Henry’s constants of CO₂ and the impurity. The Henry’s constant is the equilibrium constant of the Langmuir isotherm in the low-pressure limit, where the Langmuir expression reduces to a linear expression (i.e., \( \theta \approx K_H P \)).

Notice that the term \( K_L(\theta)P \) in eq 3 will be negligible as the equilibrium constant for the adsorption on a Mg²⁺ site is significantly larger than the one on the Linker site, so the Henry’s constant for each gas is defined as the zero-coverage \( K_{Mg^{2+}} \). This magnitude is directly related to the adsorbate/substrate affinity, which makes important the analysis of Henry’s constant differences between the desired product (i.e., CO₂) and the impurities (i.e., SO₂), trying to find the optimal working temperature, where CO₂ selectivity is maximized with respect to SO₂.

Figure 6 shows the evolution of Henry’s constants with temperature, as obtained from the DFT/DSL model, for CO₂ adsorption compared with N₂ and SO₂. As it can be seen, Henry’s constant for CO₂ is high enough to be selectively adsorbed onto Mg-MOF-74 in a binary mixture with N₂, but it is not high enough to prevent poisoning from SO₂. However, the CO₂/SO₂ Henry’s ratio increases monotonically with temperature. This implies that high temperatures could improve the Mg-MOF-74 selectivity towards CO₂ in a mixture with SO₂. Since from CO₂ and SO₂ isotherms (Figure 3) can be concluded that desorption of CO₂ (e.g., by decreasing pressure) is less energy intensive than for SO₂, an optimal separation of both gases implies a major adsorption of CO₂ onto the Mg-MOF-74. Therefore, working at very high temperatures is advisable (Figure 6), but it would also lead to a lower overall uptake, decreasing the effectiveness of this material towards CO₂ capture (Figure 4). To compare the limit cases studied, Henry’s constants of CO₂ and SO₂ are approximately 26 and 53,600 1/atm, respectively, at 293 K, and 0.5 and 38 1/atm at 373 K. These values mean that the affinity of Mg-MOF-74 for SO₂ is more than 2,061 times higher than for CO₂ at 293 K, whereas it is only 76 times higher at 393 K. On the other hand, the total uptake of CO₂ when increasing temperature is approximately reduced from 8.5 mol/kg at 293 K to 3.5 mol/kg at 393 K. However, as the Henry’s constants ratio improves CO₂ separation more rapidly than the decrease of uptake with
temperature rise, the best separation of CO\textsubscript{2} in a mixture containing SO\textsubscript{2} traces will be at higher temperatures (i.e., > 373 K according to our analysis). Nevertheless, the efficiency of this separation will be very low because at any studied temperature SO\textsubscript{2} Henry’s constant is higher than CO\textsubscript{2}, so Mg-MOF-74 still preferentially adsorbs SO\textsubscript{2}. For this reason, it is strongly recommended to remove SO\textsubscript{2} from a post-combustion flue gas mixture before employing Mg-MOF-74 as adsorbent material for CO\textsubscript{2} capture and separation.

3.5. Study of SO\textsubscript{2} Effects in CO\textsubscript{2} separation from Gas Mixtures using Mg-MOF-74. The typical temperature and pressure conditions for a post-combustion flue gas are 313-333 K and 1 atm, respectively,\textsuperscript{67} with a composition for a coal-fired power plant containing 70–75% N\textsubscript{2}, 15% CO\textsubscript{2}, 3-4 % O\textsubscript{2}, 5–7% water and traces of other species\textsuperscript{68} (500 ppm NO\textsubscript{x} and up to 2,000 ppm SO\textsubscript{2} when burning high-sulphur coals\textsuperscript{69}). The SO\textsubscript{2} poisoning effect onto Mg-MOF-74 was evaluated assuming a ternary mixture containing CO\textsubscript{2}, N\textsubscript{2} and SO\textsubscript{2}. The total uptake of the three gases at a total pressure of 1 atm was compared for different SO\textsubscript{2} impurity concentrations, which varied from a few tenths ppm up to 1 mol %, maintaining CO\textsubscript{2} in 15% and N\textsubscript{2} as the surplus. It was assumed that the complex flue gas mixture does not contain water because it was dried in a previous step before adsorption, and O\textsubscript{2} was neglected because it behaves very similar to N\textsubscript{2} when adsorbed onto MOFs, according to previous reported results.\textsuperscript{35,70}

The total uptake of CO\textsubscript{2}, N\textsubscript{2} and SO\textsubscript{2} was evaluated by varying the percentage traces of SO\textsubscript{2}, using a multicomponent dual-site Langmuir model for gas mixtures based on DFT/DSL model. Thus, the equilibrium coverage of a species (θ\textsubscript{j}) at a partial pressure \(P_j\) in a ternary mixture with \(j = \text{CO}_2, \text{N}_2\) or SO\textsubscript{2} is calculated by using eq 10. As this expression only refers to the coverage of a single species, but it depends on the coverage of the three components of the mixture, three equations (one for species) have to be solved simultaneously in an iterative process until convergence of the three coverages.

\[
\theta_j = \chi_{\text{Mg2+}} \theta_{j, \text{Mg2+}} + \chi_L \theta_{j, L} = \\
= \chi_{\text{Mg2+}} \left( \frac{K_{j, \text{Mg2+}}(\theta_j) P_j}{1 + \sum_{i=\text{CO}_2,\text{N}_2,\text{SO}_2} [K_{i, \text{Mg2+}}(\theta_i) P_i]} \right) + \chi_L \left( \frac{K_{j, L}(\theta_j) P_j}{1 + \sum_{i=\text{CO}_2,\text{N}_2,\text{SO}_2} [K_{j, L}(\theta_i) P_i]} \right)
\] (10)
The multicomponent DFT/DSL model of eq 10 implicitly considers the thermodynamic equilibrium competition between different species for each adsorption site. However, the DFT/DSL model is currently developed for single species because it only considers the effect of Mg$^{2+}$ coverage between molecules of the same gas species (i.e., the interactions between molecules of the same type). This implies that some lateral interactions are still missing in this model (i.e., the interactions between molecules of different type), which may lead to small deviations in the region where there are two or more gases with non-negligible adsorption. Although future efforts in building the complete set of interactions would refine the model (i.e., obtaining the variation of $\Delta G_{i,ads}$ with the coverage of different species), the main results are expected not to change significantly due to the large difference in SO$_2$/CO$_2$ affinity for the Mg-MOF-74.

Figure 7 shows the isotherms of different ternary mixtures calculated at 313 K with eq 10. Three concentrations were selected to show the behaviour of the gas adsorption with the presence of SO$_2$ impurities at conditions where i) SO$_2$ is too diluted to affect CO$_2$ adsorption (e.g., 0.005% SO$_2$), ii) SO$_2$ is at a concentration capable of affecting some sites in Mg-MOF-74 (e.g., 0.02% SO$_2$) and iii) SO$_2$ concentration is high enough to almost completely poison Mg-MOF-74 (e.g., 0.1% SO$_2$). As it can be seen, at impurity concentrations close to 0.02% the SO$_2$ uptake is very similar to the CO$_2$ uptake, so even at this low concentration, SO$_2$ strongly competes with CO$_2$, whereas N$_2$ uptake remain close to zero at all SO$_2$ concentrations. To locate the exact concentration of SO$_2$ in the flue gas mixture that surpasses CO$_2$ in uptake, several adsorption isotherms in perfect crystal Mg-MOF-74 were calculated for different % SO$_2$. The uptake at a total pressure of 1 atm for different % SO$_2$ are collected in Figure 8, where we observe that CO$_2$ content in Mg-MOF-74 decreases when increasing SO$_2$ percentage, with a negligible N$_2$ adsorption in all range. The change of adsorption behaviour (i.e., when Mg-MOF-74 adsorbs more SO$_2$ than CO$_2$) occurs in a reduced range of concentrations, being the crossing point between the CO$_2$ and SO$_2$ uptakes approximately at 0.020/0.025 % SO$_2$ at 313 K. However, these results are affected by temperature, as it can be seen also in Figure 8, where the uptake at 1 atm and 353 K is significantly lower for all gases than the uptake at 313 K. The crossing point between CO$_2$/SO$_2$ uptake also moves onto higher % SO$_2$ denoting an increase of CO$_2$-over-SO$_2$ selectivity when increasing temperature. For this reason, additional work was made to analyse the effect of SO$_2$ poisoning with temperature. Similar plots to Figure 8 were built using the multicomponent DFT/DSL
model from 293 K up to 373 K and the % CO₂ in the adsorbed phase was analysed. The results are collected in Figure 9, where the low temperature / low % SO₂ region presents the highest % of adsorbed CO₂. Increasing temperature reduces CO₂ adsorption, up to 75-50% at higher temperatures. On the other hand, increasing % SO₂ in the gas mixture reduces enormously the % CO₂ in the adsorbed phase; for example, at 313 K and 0.002% SO₂ presents a % CO₂ higher than 90% whereas at 313 K and 0.02% SO₂ the % CO₂ is reduced to approximately 50%.

3.6. Analysis of some Swing Adsorption Techniques for Optimal CO₂ Separation. The previous section treated the effect of SO₂ as an impurity of a CO₂/N₂ mixture in an adsorption process on Mg-MOF-74, showing that a low concentration of SO₂ in the flue gas mixture (i.e., e.g., 0.020/0.025 % SO₂ at 313 K) was enough to significantly adsorb more SO₂ than CO₂. However, in commercial gas separation/purification processes a regeneration of the sorbent bed is required for reuse in further adsorption cycles. These cycles are typically accomplished with a desorption step, where not all adsorbed gases can be effectively desorbed, performed by i) decreasing pressure (Pressure Swing Adsorption, PSA, or Vacuum Swing Adsorption, VSA), ii) increasing temperature (Temperature Swing Adsorption, TSA) or iii) by application of electrical current (Electric Swing Adsorption, ESA). Among these methods, TSA and VSA are particularly promising processes for post-combustion CO₂ capture, owing to difficulties with compressing large volumes of flue gas streams.

In VSA the standard adsorption/desorption cycle is done at constant temperature (e.g., 313 K) but decreasing the pressure from 1 atm (adsorption pressure) to about 0.1 atm (desorption pressure). However, in TSA the standard cycle is done at constant pressure (e.g., 1 atm) but increasing temperature from 313 K (adsorption temperature) to 373-443 K (desorption temperature). In this section, we analysed these methods, considering VSA cycle from 1 atm (adsorption pressure) to 0.1 atm (desorption pressure) and TSA from 313 K (adsorption temperature) to 373 K (desorption temperature). These two cycles can also be combined onto a VTSA process where the adsorption is done at 1 atm and 313 K and the desorption process is carried out 0.1 atm and 373 K (i.e., from atmospheric pressure and low temperature to low pressure and high temperature).

Two different evaluation criteria were considered in this work to analyze the CO₂ recovery performance in such swing adsorption processes: i) the working capacity and ii)
the composition of the outlet mixture. The former represents the amount of gas (e.g., CO$_2$) that can be recovered after an adsorption/desorption cycle. This parameter is generally more relevant than the total uptake at the adsorption pressure, because not all the gas adsorbed onto a material can be effectively recovered. The working capacity ($W_j$) of a selected component in the mixture (e.g., CO$_2$) is calculated from the difference between the equilibrium uptake under adsorption and desorption conditions. The adsorption value can be obtained directly from uptake at 1 atm and 313 K of the mixture calculation and the desorption value is obtained by multiplying the pure uptake at desorption conditions by the composition in the adsorbed phase, as done in our previous work. This approach is necessary for high SO$_2$ content, where impurity uptakes are not negligible, and allows more realistic results than those found in the literature based on pure adsorption data. 

Figure 10 shows the CO$_2$ working capacities for the selected TSA, VSA and VTSA processes as a function of the % SO$_2$ at the inlet mixture. The black line in Figure 10 represents the maximum working capacity of CO$_2$ that can be accomplished, which coincides with the total uptake in Mg-MOF-74 at 313 K and 1 atm. The VSA process recovers only 1 mol/kg of CO$_2$ per adsorption/desorption cycle at 0.001% SO$_2$ in contrast to the 6.4 mol/kg of the ideal maximum recovery. The TSA process recovers around 2 mol/kg of CO$_2$ per cycle, which is substantially higher than the VSA, but not efficient enough to accomplish CO$_2$ recovery from Mg-MOF-74. Finally, the VTSA presents a very high working capacity (i.e., 5.9 mol/kg of CO$_2$ per cycle at 0.001% SO$_2$), which means that over 90% of adsorbed CO$_2$ can be effectively recovered. All working capacities, as well as the ideal maximum recovery, are reduced by the % SO$_2$ at the inlet mixture, but the relative behaviours among the three processes remain equivalent, making VTSA a promising technique for this material.

On the other hand, the composition of the outlet mixture (i.e., purity) is an important variable to consider, especially when is possible to reuse the captured CO$_2$ for other applications. The composition at the outlet: $Y_{j}^{out}$ (do not confuse with the composition in the adsorbed phase: $Y_{j}^{ads}$, or the composition at the inlet: $Y_{j}^{in}$) can be calculated as the relationship between working capacity of the desired component and the sum of working capacities of all components in the mixture (eq. 11).

$$Y_{j}^{out} = W_{j} / \sum_{i} W_{i}$$  \hspace{1cm} (11)
In Figure 11, the composition of the outlet stream as a function of the % SO₂ at the inlet can be seen for the three-selected adsorption/desorption processes. VSA is the cycle that presents the lowest \( Y_{CO_2}^{out} \) along the whole range of \( Y_{SO_2}^{in} \), and its purity is reduced when increasing the amount of SO₂ at the inlet mixture. However, \( Y_{SO_2}^{out} \) will be zero in most cases because this gas has a very strong affinity for Mg-MOF-74 and once adsorbed it cannot be desorbed by only reducing pressure up to 0.1 atm. On the other hand, TSA yields a higher CO₂ purity, but the outlet starts containing important amounts of SO₂ at \( Y_{SO_2}^{in} > 0.2\% \). Finally, the studied VTSA process presents the highest \( Y_{CO_2}^{out} \) at low \( Y_{SO_2}^{in} \), which remains almost constant up to 0.03% SO₂ at the inlet mixture. At higher \( Y_{SO_2}^{in} \) the VTSA outlet stream becomes strongly poisoned by SO₂ making impossible the CO₂ recovery for further processes.

This analysis shows that VTSA is the most promising cycle at the studied conditions, being around three times more effective than TSA or six times more effective than VSA, regarding working capacities. Even though VTSA is the most expensive process, because it includes a TSA combined with a VSA cycle, the recovery is very large in comparison to the other cycles. With regard to the purity, VTSA also presents the largest \( Y_{CO_2}^{out} \) with values close to 95% of CO₂ up to \( Y_{SO_2}^{in} = 0.03\% \). For higher amounts of \( Y_{SO_2}^{in} \) TSA is preferable up to 0.3% SO₂ and VSA for \( Y_{SO_2}^{in} > 0.3\% \). However, the working capacities at these SO₂ concentrations are too low to be effectively used in CO₂ separation.

It is important to notice that although the % of adsorbed CO₂ on Mg-MOF-74 (\( Y_{CO_2}^{ads} \)) at \( Y_{SO_2}^{in} = 0.03\% \) and 313 K is approximately 30% (Figure 9), the VTSA outlet stream contains a 95% of CO₂ (Figure 11) and a 5% of N₂ (i.e., 95% purity). This means that CO₂ could be successfully recovered and separated from the flue gas mixture using VTSA if \( Y_{SO_2}^{in} \leq 0.03\% \) even if the MOF structure contains a large amount of SO₂, because it is not desorbed at the desorption step.
4. CONCLUSIONS

This work studies the adsorption of some pure cases (i.e., CO$_2$, N$_2$ and SO$_2$) on Mg-MOF-74 absorbent, developing a dual-site Langmuir model based on own periodic DFT calculations and a mean-field approximation for the inclusion of the lateral interactions, considering the effect of the surface coverage in the thermodynamic functions of adsorption. Our model, although simplified in the use of DFT data, presents adsorption isotherms and isosteric heats of adsorption in good agreement with available experimental data and with previous more accurate but also more complex ab initio models.

An extension of this model to treat gas mixtures is also presented and applied to post-combustion gases (i.e., CO$_2$/N$_2$/SO$_2$), considering the effect of SO$_2$ as impurity. It was shown that SO$_2$ concentrations as low as 0.02% in the flue gas mixture are enough to achieve higher uptakes than CO$_2$ on Mg-MOF-74 at 313 K. This low concentration slightly increased with temperature, allowing us to obtain the optimal working conditions where Mg-MOF-74 can still adsorb mainly CO$_2$ as a function of temperature and pollutant concentration.

Three different swing adsorption processes (i.e., TSA, VSA and VTSA) were analysed to determine the efficiency of the adsorption/desorption cycle through working capacities and the purity of the recovered CO$_2$. It was shown how VTSA outperforms the selected TSA and VSA cycles in both properties, especially at low % of SO$_2$ in the flue gas mixture. High amounts of SO$_2$ reduce the working capacity of CO$_2$ as well as its purity at the outlet, making unpractical CO$_2$ recovery with Mg-MOF-74.

Finally, future work should be devoted to build a more complex model in order to obtain multicomponent DFT/DSL mixture isotherms, which account for the complete set of crossed lateral interactions between all species in the mixture. Also, additional species should be studied (e.g., O$_2$, NO$_2$, NO,…) and their poisoning effects in post-combustion flue gas mixtures.
ASSOCIATED CONTENT

* Supporting Information

Details of the determination of thermodynamic functions by using DFT calculations and statistical thermodynamics. $\Delta G_{\text{ads}}$ dependence with temperature at zero-coverage and full Mg$^{2+}$ coverage.

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NOTES

The authors declare no competing financial interest.

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Tables

**Table 1.** Zero-coverage DFT adsorption energies, thermodynamic functions and equilibrium constants derived from single CO$_2$, N$_2$ and SO$_2$ molecule adsorption processes on both Mg$^{2+}$ and Linker sites. The values in parentheses were obtained considering the effect of Mg$^{2+}$ full coverage for both $i$ = Mg$^{2+}$ and $i$ = Linker sites. All values are shown in kJ/mol at a temperature of 298 K, except the equilibrium constant which has units of 1/atm.

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<th>CO$_2$</th>
<th>N$_2$</th>
<th>SO$_2$</th>
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<td>Mg$^{2+}$</td>
<td>Linker</td>
<td>Mg$^{2+}$</td>
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<td>0.1931 (0.4576)</td>
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**Table 2.** Enthalpy and Gibbs free energy of adsorption of a CO$_2$ molecule in the Mg$^{2+}$ and Linker sites at zero-coverage and two temperatures (i.e., 298 K and 343 K) obtained by periodic DFT calculations in comparison to the same magnitudes calculated by Sillar et. al., 40 (in parentheses). All results are in agreement within the chemical accuracy of 4 kJ/mol.

<table>
<thead>
<tr>
<th></th>
<th>CO$_2$ at 298 K</th>
<th>CO$_2$ at 343 K</th>
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<td></td>
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<td>$\Delta G_{ads}$</td>
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<td>6.3 (5.1)</td>
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Figures

Figure 1. Fully relaxed structure of Mg-MOF-74 optimized by the periodic DFT calculations.

Figure 2. (a) Representation of a Mg-MOF-74 pore, where two CO$_2$ molecules (in orange) are adsorbed onto the Mg$^{2+}$ sites and two CO$_2$ molecules (in blue) are adsorbed onto the Linker sites, which also weakly interact with a Mg$^{2+}$ cation stabilizing the adsorption site. The squared region in (A) is zoomed in (B) and slightly turned to see that the adsorption site distribution is alternated (i.e., Linker-Mg$^{2+}$-Linker-Mg$^{2+}$).
Figure 3. Adsorption isotherms predicted for pure CO$_2$ (Top), N$_2$ (Middle) and SO$_2$ (Bottom) on Mg-MOF-74. DFT/DSL isotherms accounting for lateral interactions are represented in solid lines: red for the perfect crystal and blue for 81%-availability isotherm. Results from Sillar et al., 40,41 with the more complex model are given for validation (in dashed magenta). Also, experimental results from data set 1 (●) 56,65,66 and data set 2 (○) 65 are used to compare CO$_2$ and N$_2$ isotherms at 298 K.
Figure 4. Temperature effect on the pure component 81%-availability DFT/DLS adsorption isotherms (solid lines) compared with experimental results from Mason et al., 26 (dots). Different colours represent different temperatures ranging from 293 K to 373 K.
Figure 5. DFT/DSL variation of isosteric heat of adsorption ($q_{st}$) with coverage for a perfect crystal (red), 81%-availability of sites (blue) for CO$_2$, N$_2$ and SO$_2$ obtained with eq 7. The results obtained with Clausius-Clapeyron equation (eq 8) are not shown because they are almost identical to the ones obtained by eq 7. Experimental reported results of Dietzel et al., (•) $^{60}$ and Queen et al., (○) $^{51}$ are indicated when available for comparison.
Figure 6. CO$_2$, N$_2$ and SO$_2$ Henry’s constants at different temperatures from 293 K to 373 K, where the reduction of SO$_2$ affinity towards Mg-MOF-74 can be observed.
Figure 7. DFT/DSL isotherms for the ternary mixture obtained with the multi-component dual-site Langmuir model (eq 10) at 313 K with three different initial SO₂ concentrations (i.e., from lower concentration at top, to higher concentration at bottom) keeping CO₂ at 15% and N₂ as the surplus.
**Figure 8.** Calculated gas adsorption uptake at different mol % SO\(_2\) in ternary gas mixtures with 15% CO\(_2\), and N\(_2\) as the surplus. DFT/DSL model results were obtained with the multicomponent dual-site Langmuir model (eq 10). The results are shown at 313 K (solid lines) according to a typical post-combustion flue gas temperature and at 353 K (dashed lines) to analyse the temperature effect on the CO\(_2\)/SO\(_2\) uptake.

**Figure 9.** Variation of the % CO\(_2\) in the adsorbed phase at different temperatures and SO\(_2\) concentrations of the flue gas. The red region shows the conditions where almost the whole structure is occupied by CO\(_2\), whereas green and blue regions show where SO\(_2\) importantly affects the CO\(_2\) adsorption (i.e., close or past the crossing CO\(_2\)/SO\(_2\) point in Figure 8).
Figure 10. CO$_2$ Working capacities for the selected VSA (green), TSA (red) and VTSA (blue) processes as a function of % SO$_2$ in the inlet flue gas at 313 K. The black line corresponds to the ideal situation where all CO$_2$ adsorbed on the structure would be desorbed, that is, the CO$_2$ uptake shown in Figure 8 at 313 K.
Figure 11. CO$_2$, N$_2$ and SO$_2$ composition at the outlet stream as a function of the % SO$_2$ in the inlet flue gas mixture for the selected TSA (top), VSA (middle) and VTSA (bottom) processes. The adsorption/desorption conditions can be seen in each graph.
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34
Coordination Sites
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Chabal, Y. J. Interaction of Acid Gases SO
Phys. Chem. C
Unsaturated Metal
Design.
Site Metal
3
Waals Density Functionals.
Experiment
New Jersey, 2010

