Thermodynamic and Kinetic Characterization of Yellow Tuff for CO$_2$ Adsorption

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CO$_2$ adsorption on a yellow tuff has been studied, by performing dynamic breakthrough experiments in fixed bed, focusing on the thermodynamics and kinetics of the process. The effect of both temperature (25 – 150 °C) and CO$_2$ partial pressure (0.01 – 0.20 atm) has been assessed. The CO$_2$ adsorption isotherms in the low pressure region typical of combustion flue gases are more accurately described by the Freundlich equation than by the Langmuir one, thus indicating a multilayer and heterogeneous surface binding. The obtained values of the main thermodynamic parameters suggested that the adsorption process is spontaneous, exothermic and physical in nature. The pseudo-first order kinetic model better fitted the experimental data at all the investigated adsorption temperatures than the pseudo-second order does.

1. Introduction

Among all the available post-combustion capture technologies, adsorption using solid sorbents is characterized by low regeneration energy consumption, selectivity, easiness in handling, no liquid waste streams and applicability over a relatively wide range of operating temperatures (Raganati et al., 2016). However, the choice of the adsorbent material represents a critical point for the success of this approach (Gargiulo et al., 2016). Indeed, the sorbent should combine low cost with versatility and good performances at low CO$_2$ pressure (Ramli et al., 2014), up to 0.2 atm in typical post-combustion conditions (Raganati et al., 2015). In this context, great attention has been focused on zeolites. Synthetic zeolites are highly ordered microporous crystalline materials, synthetized with a very specific and suitable molecular cell size, giving them the intrinsic capability to adsorb polar species (Siriwardane et al., 2001). However, their high synthesis cost and the environmental footprint represent a negative contribute to their sustainability (Siriwardane et al., 2001). A possible alternative is provided by natural occurring zeolites, as they are available in large quantities in the natural composition of different types of rocks (Ackley et al., 2003). Therefore, they are low-cost sorbents, not needing "ad hoc" synthesis, and environmental-friendly, not introducing additional CO$_2$ in the environment (Ackley et al., 2003). Their abundance and low or null price, somehow, offset some unavoidable drawbacks such as variable composition that may change even in a single deposit, low purity and likely poorer separation performance compared to the more-performant synthetic zeolites (Ackley et al., 2003). In this framework, the volcanic tuffs are the most valuable deposits of natural zeolites and they are characterized by the presence of different minerals, such as: clinoptilite, mordenite, chabazite, quartz, cristobalite, feldspar, etc. (Colella, 2008). Nonetheless, the literature about the use of natural tuff as CO$_2$ adsorbent at low pressure is still lacking. After the selection of the adsorbent material, a combined study of the equilibrium and kinetics is necessary for the design of the specific adsorption system (such as pressure swing and temperature swing). Indeed, the accurate mathematical representation of both the adsorption equilibrium and kinetics is crucial for the identification of the adsorption performances, by providing useful insight into the adsorbate-adsorbent interactions (Raganati et al., 2018). In particular, a good adsorbent should provide the right compromise between high equilibrium adsorption capacity and fast kinetics that are requisites for process implementation (Raganati et al., 2018). This work is aimed at investigating the low-pressure CO$_2$ adsorption on a natural zeolite tuff, with particular attention to its mechanism, in terms of thermodynamics and kinetics. Dynamic breakthrough tests have been carried out in a in a lab-scale fixed bed reactor. In particular, the tuff was tested

at different adsorption temperatures (25-150 °C) and CO_2 partial pressures (0.01 – 0.20 atm). Then, the Langmuir and Freundlich isotherm models have been used to fit the experimental equilibrium data in the low CO_2 pressure region typical of a combustion flue gas. The evaluation of the most important thermodynamic properties, i.e. the standard Gibbs free energy, enthalpy change, entropy change and isosteric heat of adsorption, has provided insights into the feasibility and strength of adsorbate–adsorbent interaction. Pseudo-first and pseudo-second order kinetic models have been used to fit the experimental CO_2 uptake data, thus obtaining the rate of CO_2 adsorption for possible equipment design.

2. Experimentals

Materials and experimental apparatus: A natural yellow tuff from Campania (I) region has been used as adsorbent material. The sample has been crushed and sieved to obtain a 400-600 μm fraction. Prior to the CO_2 adsorption study, the tuff physical and structural properties have been characterized. The internal porosity and the absolute density of the material have determined by employing mercury intrusion porosimetry (MIP, ThermoFinnigan 240). XRD analysis has provided the phase composition of the tuff by using a Bruker D8 Advance powder diffractometer with Cu Kα radiation. The CO_2 dynamic breakthrough tests were carried out at atmospheric pressure in a laboratory-scale fixed bed reactor (ID = 10 mm, column length = 600 mm). More detailed information can be found elsewhere (Gargiulo et al., 2018). Separate high purity N_2 and CO_2 cylinders (99.995% vol.) are used to prepare the gas feed, using two mass flow controllers (Brooks 8550S) to set and control the inlet flowrates. The analysis system consists of a continuous gas analyzer equipped with an infrared detector (ABB AO2020, URAS 14). In a typical adsorption test, the sorbent (5 g, corresponding to about 5 cm of bed height) is subjected to a drying/cleaning step by flowing N_2 (15 L h^{-1}) for 60 min at 150 °C. Afterwards, the sorbent is pre-conditioned for about 10 min by setting the temperature (25, 40, 70, 100 and 150 °C) to the desired value and fluxing 15 L h^{-1} of N_2 through the system. This is followed by the adsorption step in which 15 L h^{-1} of the CO_2/N_2 gas mixture (1, 3, 5, 10, 15 and 20 % vol. of CO_2) is fed through column. By continuously monitoring the CO_2 concentration in the outlet stream until saturation of the bed (i.e. the outlet CO_2 concentration approached the inlet value) the breakthrough curves are obtained.

Adsorption thermodynamics: Langmuir and Freundlich models have been employed to fit the experimental adsorption isotherms of the tuff. The Langmuir model is the simplest theoretical model to describe monolayer adsorption onto homogeneous surfaces (i.e. the adsorption sites are equivalent from an energetic point of view) (Raganati et al., 2018) and it is based on the following mathematical expression:

$$q_e = q_L \frac{K_L P_{CO_2}}{1 + K_L P_{CO_2}} \qquad (1)$$

where q_e (mmol g^{-1}) is the amount of CO_2 adsorbed per mass of sorbent at equilibrium, q_L (mmol g^{-1}) is the maximum monolayer adsorption capacity of the adsorbent, PCO_2 (atm) is the equilibrium pressure of the gas adsorbed, whilst K_L (atm^{-1}) is the Langmuir adsorption constant or affinity constant. The Freundlich model is the first empirical equation to describe non-ideal multilayer adsorption onto heterogeneous surfaces and it assumes that the adsorption energy exponentially decreases as the number of available adsorption sites decreases (Raganati et al., 2018). Its mathematical expression is:

$$q_e = K_F P_{CO_2}^{1/n} \qquad (2)$$

where K_F is the Freundlich isotherm constant (mmol g^{-1} atm$^{-1/n}$) and n is the heterogeneity factor (Freundlich coefficient). The ratio 1/n is the Freundlich intensity parameter and it is a measure of the adsorbate/adsorbent binding energy and surface heterogeneity (Freundlich, 1906). Moreover, the magnitude of 1/n gives insight on whether the process is favorable or not, the adsorption being favorable at 1/n < 1 (Freundlich, 1906). The quality of the isotherm fit by Lamgmuir and Frenundlich models to experimental data has been assessed by evaluating the coefficient of correlation, R^2, and the HYBRID error function (Raganati et al., 2018). The most important thermodynamic parameters, i.e. the standard Gibbs free energy change (ΔG^0, kJ mol^{-1}), the enthalpy change (ΔH^0, kJ mol^{-1}), and the entropy change (ΔS^0, kJ mol^{-1}), have been evaluated by combining the thermodynamic laws with the experimental data obtained from the Langmuir isotherms and by applying the van't Hoff equation, in order to obtain information on the nature of the adsorbent-adsorbate interactions and on the energetic heterogeneity of the solid surface (Raganati et al., 2018). Also the isosteric heat of adsorption (Q_{st}), defined as the heat of adsorption at constant amount of adsorbed adsorbate, has been evaluated since it can provide an estimation of the strength of molecular-scale interactions between the adsorbate molecules and the adsorbent surface (Raganati et al., 2018). Q_{st} (kJ mol^{-1}) at a given q_e can be calculated, after integrating the Clausius–Clapeyron equation, from the slopes of the plot of $\ln P_{CO_2}$ against $1/T$ at a fixed specified adsorbed amount of CO_2 (Raganati et al., 2018).

Adsorption kinetics: Among the kinetic models available in the literature, pseudo-first order and pseudo-second order models are the simplest and most extensively used ones (Raganati et al., 2018). The mathematical expression pseudo-first order kinetic model is given by (Raganati et al., 2018):

$$q_t = q_e[1 - exp(-k_f t)] \tag{3}$$

where q_t (mmol g^{-1}) is the amount of CO_2 adsorbed per mass of sorbent at the time t, and k_f (min^{-1}) is the rate constant of first-order sorption. This model can properly describe a reversible type of adsorbate/adsorbent interactions, as the case of CO_2 adsorption on physical adsorbents like activated carbons and zeolites (Loganathan et al., 2014). The mathematical expression of the second order kinetic model is (Loganathan et al., 2014):

$$q_t = \frac{q_e^2 k_s t}{1 + q_e k_s t} \tag{4}$$

where k_s (g mmol^{-1} min^{-1}) is the second order rate constant. This model assumes that, besides weak physical interactions, adsorption is also associated to chemical adsorbate/adsorbent interactions, thus being generally most suited to describe chemisorption (Loganathan et al., 2014). The fitting quality of the kinetic models to the experimental data has been then assessed by R^2 and HYBRID (Raganati et al., 2018).

3. Results and discussions

Materials characterization: The tuff is characterized by a rather high level of cristallinity, with characteristic reflection peaks of chabazite located at 2θ=20.45, 22.86, 24.61, 30.40, and 30.73, typically abundant in natural zeolites, together with other impurities (feldspar, quartz, calcite, etc.) (Ammendola et al., 2017). Detailed information regarding the morphology, chemical composition and pore distribution of the tuff can be found elsewhere (Ammendola et al., 2017), also including SEM and N_2 adsorption characterization. Briefly, the material is characterized by micronic cubic shaped structures, typical of the zeolites, as well as glassy regions, and it is basically microporous (7 Å < d < 20 Å) with a unimodal pore size distribution, as typically reported for zeolites. The corresponding BET surface area is 141 m^2 g^{-1}.

Adsorption thermodynamics: The fitting of the experimental data by Langmuir and Freundlich models are reported in Figure 1. Table 1 reports the values of the model parameters, R^2 and HYBRID.
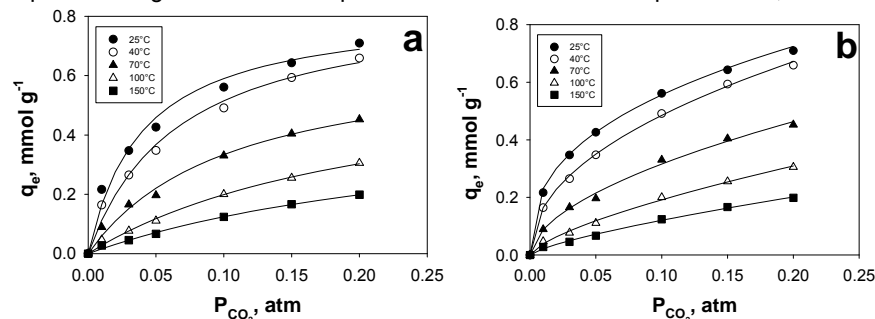

Figure 1: CO_2 adsorption isotherms fitted by: a) Langmuir model; b) Freundlich model.

Figure 1 clearly shows that both the models used in this work fitted the experimental results quite well, in line with the results obtained by other Authors with physical sorbents (Guo et al., 2006). This was also confirmed by the fact that R^2 is always larger than 0.99 and HYBRID is always lower than 0.5%. As a matter of fact, it is quite common that both Langmuir and Freundlich isotherms are able to fairly fit the same set of CO_2 adsorption data at certain CO_2 partial pressure ranges, at least from a macroscopic point of view (Monazam et al., 2013). In particular, this is true especially when PCO_2 is small (i.e. < 0.1atm, as typical of post-combustion capture applications) and q_e is also small enough to have linear shape of adsorption isotherm. As a confirmation, it clearly appears from Figure 1a that the Langmuir fitting is less accurate at lower temperatures, i.e. when q_e is larger and the adsorption isotherms moves away from the linearity. This can be ascribed to the fact that when a larger amount of CO_2 is adsorbed, it is most likely that multiple layers of CO_2 molecules are adsorbed on the sorbent surface; as a consequence, Freundlich model is able to give a better fitting. As regards the effect of temperature, Table 1 clearly shows that, when temperature is increased, the predicted values of maximum amount of CO_2 adsorbed (q_L) and adsorption isotherm constants (K_L and K_F) decreased. This is in line with the exothermicity of the CO_2 adsorption phenomenon on the tuff, i.e. it is thermodynamically favored at low temperatures. Also regarding the results obtained from the Freundlich model, n > 1 at all the investigated temperatures, which is an indication of a high level of heterogeneity of the system as long as of

good adsorption intensity (Freundlich, 1906). Also, the dependence of n on the adsorption temperature is a further confirmation of the fact that CO_2 adsorption on the tuff is favored at low temperatures, according to its exothermic in nature.

Table 1. Langmuir and Freundlich adsorption equation parameters and fitting comparison.

T,	Langmuir				Freundlich				
°C	q_L	K_L	R^2	HYBRID	k_F	n	1/n	R^2	HYBRID
25	0.826	24.988	0.994	0.526	1.341	2.616	0.382	0.999	0.035
40	0.859	14.968	0.994	0.479	1.430	2.129	0.469	0.999	0.020
70	0.684	9.526	0.994	0.352	1.128	1.808	0.553	0.999	0.076
100	0.636	4.556	0.997	0.212	0.939	1.448	0.690	0.999	0.072
150	0.493	3.373	0.998	0.129	0.665	1.347	0.742	0.999	0.055

Figure 2a reports van't Hoff plot for the natural tuff in the temperature range of 25 - 150 °C. The values of ΔH^0, ΔS^0 and ΔG^0 are listed in Table 2. ΔG^0 is always negative, thus indicating that the CO_2 adsorption process on the tuff occurs favorably and spontaneously at all the adopted adsorption temperatures. Besides that, the van't Hoff plot exhibits an increasing trend; i.e. when temperature is increased, the magnitude of ΔG^0 is decreased, which is a confirmation of the adsorption feasibility decreasing at higher temperatures. This is also in line with the above reported adsorption isotherms. ΔH^0 is also negative, which further confirms the exothermicity of the adsorption process, i.e. energy in form of heat is generated into its surroundings during the adsorptive process since new physical/chemical bonds are formed. As regards its magnitude, ΔH^0 values are lower than 20 kJ mol^{-1}, thus confirming that CO_2 adsorption on the tuff is physical in nature (Raganati et al., 2018). Finally, ΔS^0 is also negative, meaning that the disorder and randomness of the system decrease during the adsorption process. Indeed, when adsorbed on the tuff surface, the CO_2 molecules lose the freedom of movement they have in the gaseous phase (Raganati et al., 2018).
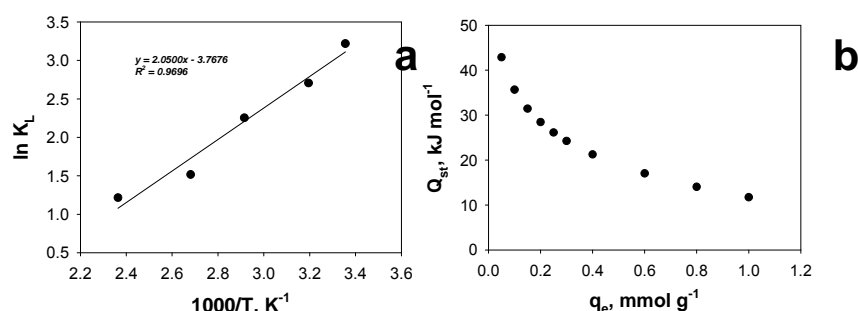

Figure 2: a) Van't Hoff plot. b) Variation of the isosteric heat of adsorption with the CO_2 loading.

Table 2. Thermodynamic properties for CO_2 adsorption on the natural tuff.

ΔH^0	ΔS^0	ΔG^0				
		18°C	40°C	70°C	100°C	150°C
-17.04	-0.031	-7.709	-7.239	-6.300	-5.360	-3.794

Figure 2b shows Q_{st} as a function of the CO_2 loading. Q_{st} ranges between 15 and 45 kJ mol^{-1} that are typical of a purely physical interaction (< 80 kJ mol^{-1}). Then, it is clear from Fig. 2b that Q_{st} decreases with increasing CO_2 surface loading, which means that the tuff is characterized by a high level of heterogeneity and that there is a variation in adsorbate-adsorbent and adsorbate-adsorbate interactions. This evidence can be explained considering that at the initial stages of adsorption, large numbers of free adsorption sites are available on the tuff surface. Therefore, the CO_2 molecules may easily come into direct contact with adsorbent surface; as a consequence, the activation energy is low and the heat of adsorption is high. As the adsorption process continues to take place, i.e. the surface coverage is increased, less and less adsorption sites are still available and, as a consequence, the adsorption of further CO_2 molecules becomes more and more difficult. Besides that, it is most likely that some kind of lateral interactions in the adsorbed layer start to take place in the form of attractive/repulsive forces between CO_2 molecules adsorbed on the tuff surface (adsorbate–adsorbate interactions) (Raganati et al., 2018). As a result, as the adsorption process proceeds, the activation energy is increased and the heat of adsorption is decreased.

Adsorption kinetics: Figure 3 presents the CO_2 transient adsorption uptakes and fractional adsorption uptake on the tuff at different adsorption temperatures (at 10%vol. of CO_2 inlet concentration), as evaluated from the experimental breakthrough curves. It is clear that adsorption kinetics and thermodynamics are differently affected by the temperature. Indeed, when temperature is increased, the CO_2 adsorption becomes faster due to enhanced kinetics and, on the contrary, the amount of CO_2 adsorbed at equilibrium is decreased due to thermodynamics limitation. In other words, the equilibrium CO_2 adsorption capacity decreases with the temperature increasing, the asymptotic values reached by the CO_2 uptake curves in Figure3a decreasing as temperatures increased, which is in line with the exothermicity of the adsorption.
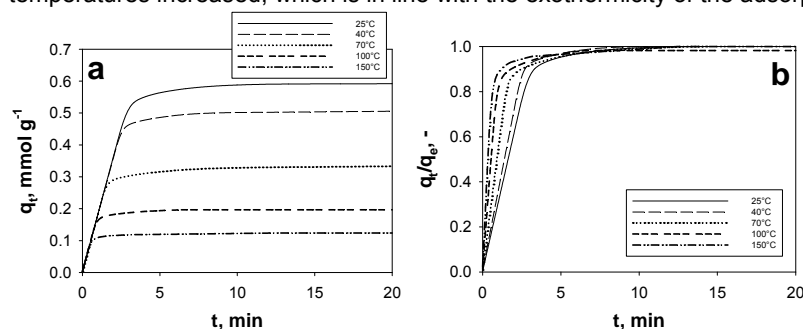

Figure 3: a) CO_2 transient adsorption uptakes; b) CO_2 fractional adsorption uptakes.

On the contrary, higher temperatures positively affect adsorption kinetics, as it is clearly shown by the curves becoming steeper (Figure 3b) with increasing temperatures, in accordance with the fastened mass-transfer and diffusion phenomena at higher values of adsorption temperatures. Then, the pseudo-first order and pseudo-second order models have been used to fit the experimental data (Figure 4). Table 5 reports the values of the kinetic constants with the relative correlation coefficients and errors.
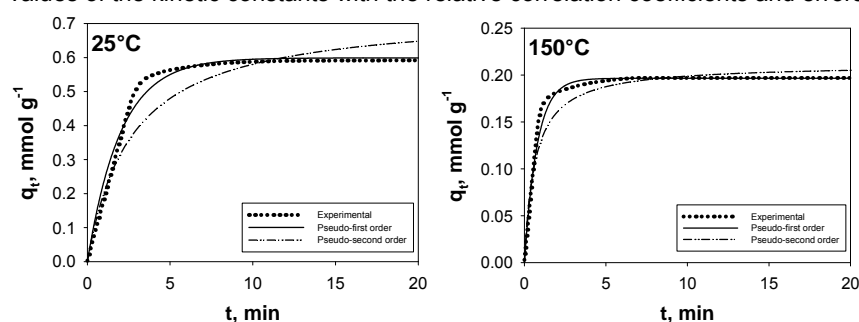

Figure 4: Experimental (dotted line) CO_2 uptake and corresponding fit to the pseudo-first (solid line) and pseudo-second (dashed line) order kinetic models at the lowest and highest investigated adsorption temperatures.

Figure 4 clearly shows that for each investigated temperature, the pseudo-first order kinetic model fits the experimental data better than the pseudo-second order kinetic model does (this shows larger deviations from the experimental data). More specifically, the pseudo-second order model tends to underestimate the CO_2 uptake in the first few minutes (t < 5 min); in contrast, this is remarkably overestimated in the last stage of the adsorption process, namely as the equilibrium is approaching. As a consequence, the pseudo-second order model significantly overestimates the equilibrium CO_2 uptake (q_e) (Table 3).

Table 3. Values of the pseudo-first order and pseudo-second kinetic model parameters and fitting comparison

T, °C	Pseudo-first order				Pseudo-second order			
	q_e	k_f	R^2	HYBRID	q_e	k_s	R^2	HYBRID
25	0.605	0.403	0.995	0.0672	0.734	0.516	0.987	0.111
40	0.513	0.476	0.997	0.0636	0.607	0.766	0.988	0.109
70	0.331	0.745	0.998	0.0432	0.372	2.173	0.989	0.084
100	0.197	1.295	0.999	0.0294	0.212	7.372	0.995	0.067
130	0.122	2.108	0.999	0.0244	0.129	21.052	0.996	0.047

In contrast to this, the pseudo-first kinetic model is capable of adequately fitting the experimental points during the entire time evolution of the adsorption. This better quality is clearly confirmed by the data reported in Table 3, in terms of higher values of R^2 and lower values of HYBRID. These results can be ascribed to the fact that

that the pseudo-first order can fairly describe adsorption processes characterized by reversible adsorbate/adsorbent surface interactions, i.e. purely physical adsorption. On the contrary, the second-order kinetic model can better describe chemisorption processes, i.e. it is a better choice when it is necessary to account for the occurrence of chemical bonding between the adsorbate and the adsorbent surface. Therefore, these results are in line with those obtained from the thermodynamic study, showing that the CO_2 adsorption on the tuff is purely physisorption. It can also be also observed that, whatever the kinetic model, the kinetic constant (k_f and k_s) increase with increasing temperatures, in line with high temperatures favoring adsorption (Table 3).

4. Conclusions

In this work CO_2 adsorption on a natural tuff has been studied focusing on the thermodynamics and kinetics of the process. Dynamic breakthrough experiments have been performed in a lab-scale fixed bed reactor. As regards thermodynamics, it is oppositely affected by temperature and pressure. Indeed, when CO_2 partial pressure is increased, the equilibrium CO_2 adsorption uptake increases, whereas it decreases when temperature is increased. The equilibrium experimental data has been fitted by Langmuir and Freundlich models. The Freundlich model provides the better results in terms of fitting quality, which suggests that CO_2 adsorption on the tuff is multilayer and happens with a heterogeneous surface binding. Then, the study of the thermodynamic parameters has shown that CO_2 adsorption on the tuff is spontaneous, exothermic and physical in nature. As the surface loading increases, the isosteric heat of adsorption decreases, which is a further confirmation of the tuff having an energetically heterogeneous surface and that some kind of lateral interactions take place among the CO_2 molecules adsorbed on the tuff surface. Then, the pseudo-first and pseudo-second kinetic model have been adopted to fit the experimental data. The pseudo-first order kinetic model is the best one, being able to provide a better quality of the fitting all the investigated adsorption temperatures.

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