CO_2 capture and storage by natural zeolites

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In the last decades, the valorization of the solid organic waste has received growing interest. The waste treatment has increased the attention towards a new renewable energy carrier: the biogas. The biogas has different composition depending on the solid waste (i.e., CH_4=65%, CO_2=30%, H_2O=1.9%, N_2=1.8%, H_2S=0.6%, O_2=0.5%, mercaptans=0.2%). Since the CO_2 amount is not negligible, it must be captured because it is one of the significant contributors to the greenhouse effect (Hijazi, Munro, Zerhusen, & Effenberger, 2016).

Over the years, several technologies were developed to abate CO_2. However, the actual capture systems are not low-cost, and the research is focusing on other possible technologies (Khraisheh et al., 2020). In this scenario, zeolites could be an interesting solution. These materials are characterized by [SiO_4] and [AlO_4]$^-$ with three-dimensional structure. Thanks to this structural conformation, the zeolite can create cavities with different pores dimensions: micropores (d < 2 nm), mesopores (2 nm < d < 50 nm) or macropores (d > 50 nm). A material with these physico-chemical properties could have application for several environmental applications, like water, soil and air decontamination (Colella, 2007).

Among the zeolites, the natural ones have received interest in academia and industry because of their potential applications and low-cost compared with the commercial (synthetic) zeolites. In particular, the clinoptilolite is the most used natural zeolite. This material can adsorb CO_2 by Van der Waals forces, and the modification of the chemical composition (i.e., by means ion exchange method) may increase the CO_2 adsorption capacity. It was demonstrated that the capacity of CO_2 removal by clinoptilolite follows the following orders: $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$ and $Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$ (Siriwardane, Shen, & Fisher, 2003).

In this study, the clinoptilolite (powder, provided by Zeolado, Greece) was used for the CO_2 capture at different temperatures, in the range 25 – 150 °C. The CO_2 adsorption tests were performed at 10 vol.% CO_2 and W/F = 7.5 g min l^{-1}. Before the tests, the clinoptilolite was pretreated at 400 °C for 2 h with N_2 flow. The results are reported in Figure 1 and Table 1. As a whole, the CO_2 adsorption capacity decreases as the temperature increases (Figure 1A). The clinoptilolite presents good adsorption capacity at low temperature (2.2 $mmol_{CO2\ adsorbed}$ g^{-1}_{clino}). Moreover, the clinoptilolite is stable for two consecutive runs (Figure 1B).

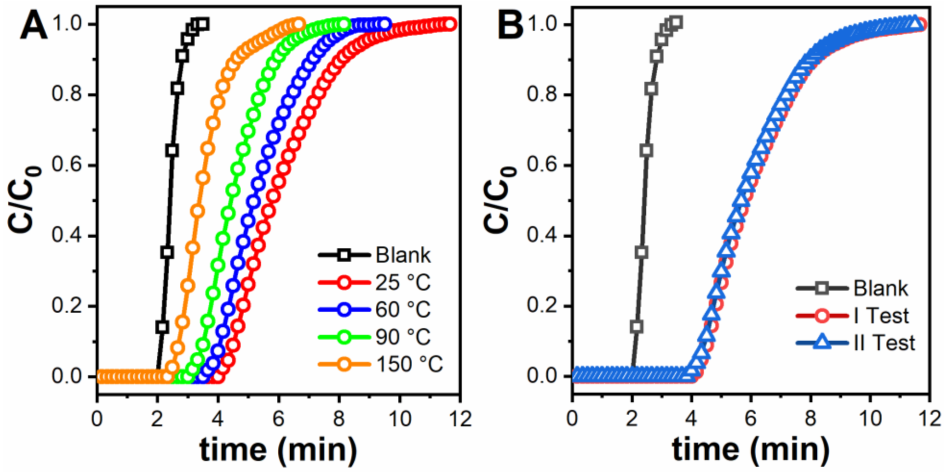

Figure 1. A) CO_2 capture over the time at different temperatures and B) stability tests (at 25 °C) for two consecutive runs on clinoptilolite powder.

Table 1. CO_2 absorbed ($mmol_{CO2\ adsorbed}$) over the clinoptilolite mass at 25, 60, 90 and 150 °C.

Temperature (°C)	25	60	90	150
CO_2 adsorbed ($mmol_{CO2\ adsorbed}$ g^{-1}_{clino})	2.2	1.8	1.3	0.7

Also, the clinoptilolite was compared with other CO_2 capture materials, as the hydrocalcite and the Linde Type A (LTA) zeolites. The LTA was ion-exchanged with Na and Ca in order to have better performances. The results are shown in Figure 2 at 25, 60, 90 and 150 °C. With the increase of the temperature, the adsorption capacity for all the samples decreases. At 25 °C, the most performing catalysts are Na- CaLTA samples, respectively, 3.1 and 3.3 $mmol_{CO2\ adsorbed}\ g^{-1}_{adorbent}$. However, at a higher temperature (150 °C), the most interesting catalyst is clinoptilolite (0.7 $mmol_{CO2\ adsorbed}\ g^{-1}_{adorbent}$), and the worst performances are represented by the hydrocalcite (0.4 $mmol_{CO2\ adsorbed}\ g^{-1}_{adorbent}$).

In conclusion, the clinoptilolite is an interesting (sustainable) material that can be used for the CO_2 capture at relatively high temperature since it is less affected by the variation of the temperature, compared to LTA-type zeolite and hydrocalcite.

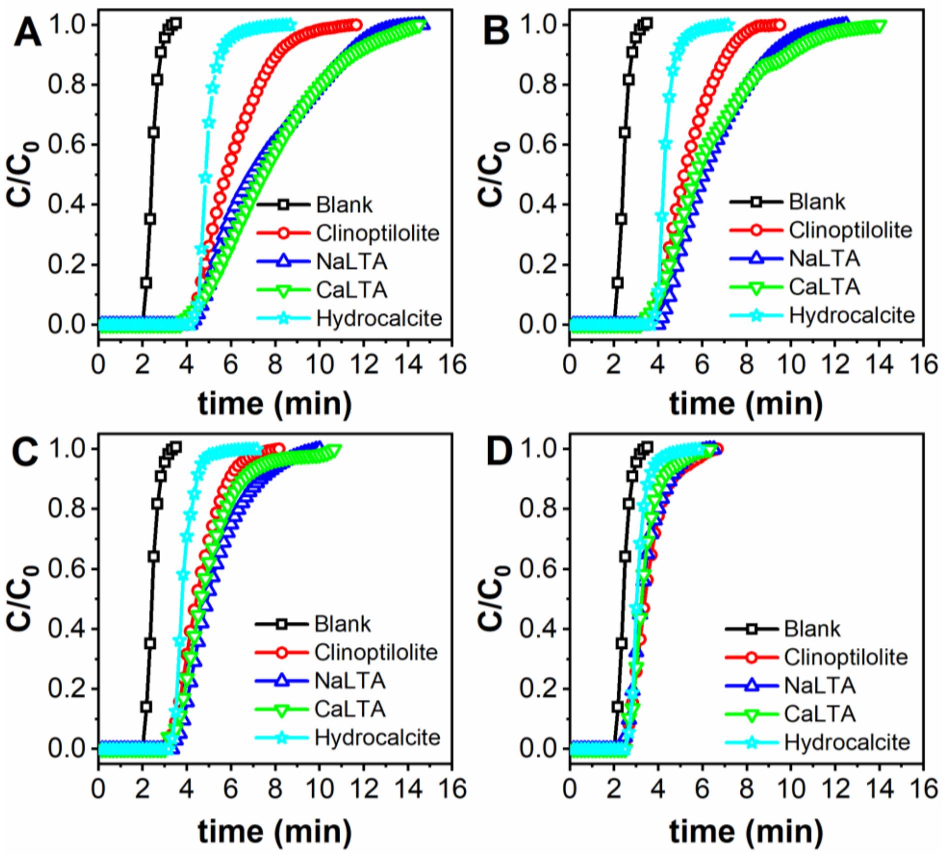

Figure 2. A) CO_2 capture at 25 °C, B) 60 °C, C) 90 °C and D) 150 °C over the time.

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