Effect of water vapour on post-combustion CO_2 adsorption

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Objectives and Novelty

The consequences of climate change are already noticeable. Even if greenhouse gas emissions were significantly reduced, global warming would continue over the coming decades and the effects would ever be perceptible in the centuries to come. For this reason, the international community is committed to achieving carbon neutrality between 2050-2100. This critical situation will require the deployment of all available technologies during this transition period.

One of the main paths towards mitigating CO_2 emissions from large point stationary sources is through the application of carbon capture and storage technologies. In recent years, considerable research effort has been devoted to this aim. CO_2 adsorption, the subject of this PhD dissertation, is among the wide variety of processes able to capture CO_2. Over the last decade, research on new low-cost adsorbent materials with a high CO_2 capture performance, particularly in post-combustion capture applications, has been very intensive. Within this context, it is of the utmost importance to evaluate the performance of the adsorbents under humid conditions and in the presence of other pollutants in the gas stream so as to assess conditions representative of real industrial applications. It was the circumstances just described that motivated this research into the effect of water vapour on post-combustion CO_2 capture as part of the present PhD thesis.

The main objective has been to address the performance of biomass-based CO_2 adsorbents in post-combustion capture conditions where the level of humidity is very high. A set of biomass-based carbons have been produced and optimised following different methodologies to enhance the selectivity towards CO_2 in the presence of water as well as to maximise CO_2 uptake under these conditions.

Results

In order to limit water vapour adsorption on activated carbons, several techniques of surface hydrophobisation and demineralisation of microporous carbonaceous adsorbents have been explored. Heat treatment removed most of the oxygen on the carbon surface whereas wet impregnation with amines and acid washing increased it. Similar oxygen surface functionalities were identified in all the carbons by means of TPD tests and FTIR. Moreover, impregnation with amines successfully incorporated nitrogen functionalities by reaction with oxygen moieties of the carbon support. On the other hand, all evaluated post-treatments led to a decrease in surface area and micropore volume.

Independently of the parent carbon selected (RN1 or RN2), the overall effect of the conducted post-treatments was a decrease of water vapour adsorption in the first part of the isotherm ($P < 0.85$ kPa) (see Figure 1). In the higher pressure ranges, post-treatments also reduced the total water vapour uptake with the exception of heat treatment (RN1P) that led to an increase of 6.8% with respect to the parent carbon. Wet impregnation (RN2D5 and RN2D10, DETA loadings of 5 and 10 wt.%, respectively) was the most effective to attain an important reduction in the water vapour adsorption capacity.
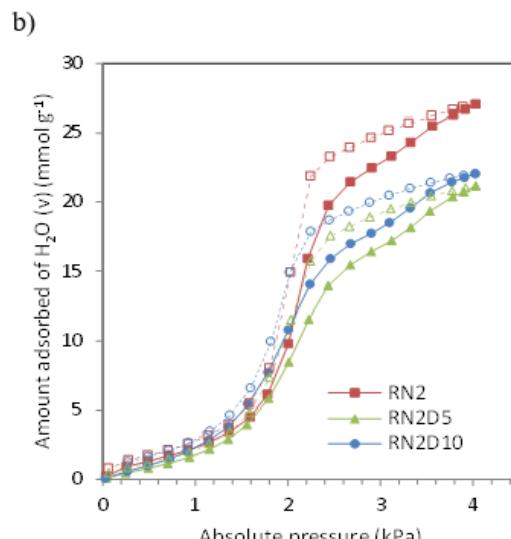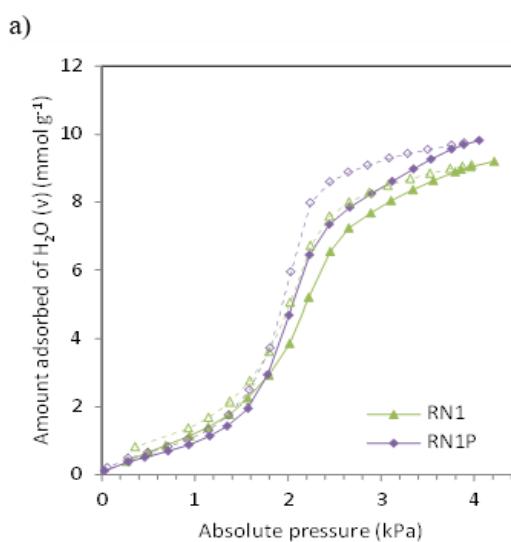
Figure 1. Water vapour adsorption isotherms at 30 °C: (a) RN1 and RN1P; (b) RN2, RN2D5, and RN2D10 (full symbols and continuous lines correspond to the adsorption branch, and empty symbols and dashed lines to the desorption branch).

High-performance post-combustion CO_2 capture adsorbents have been developed by hydrothermal carbonization and CO_2 activation from spent coffee grounds. Preliminary testing showed that the CO_2 capture capacity decreased with the addition of both water and hydrogen peroxide in the HTC treatment. Response surface methodology determined the HTC temperature as the most influential parameter on the process, while no effect of the dwell time was detected (see Figure 2). The maximum value of CO_2 capture capacity at 50 °C and a CO_2 partial pressure of 10 kPa, 0.67 mmol g^{-1} (2.95 wt.%) was attained at both the lowest temperature and dwell time of HTC (120 °C, 3 h).

Analysis of the features of the two ACs produced revealed that HC-Co (HTC followed by CO_2 activation) shows superior performance for CO_2 adsorption under post-combustion capture conditions than AC-Co (single step CO_2 activation, patent ES2526259), which can only be attributed to the HTC process.
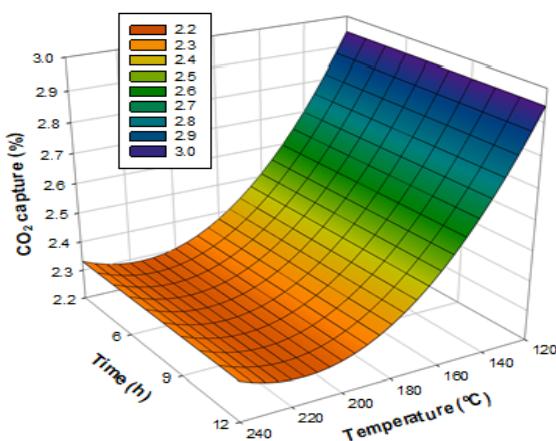
Potassium-based solid sorbent RN2K has been prepared by impregnation with K_2CO_3 (40%) on activated carbon RN2, a microporous biomass-based carbon produced in our laboratory. Impregnation of RN2 with potassium carbonate notably reduced the volume of available porosity for adsorption. The reduction of both the narrow pore size and the narrow micropore volume in RN2K caused a slight decrease in CO_2 uptake when physical adsorption was the single process involved. This was the case for the dry experiments feeding CO_2/N_2 and for the wet experiments feeding $CO_2/N_2/H_2O$ to a fresh bed of adsorbent (dynamic experiments conducted in a fixed-bed lab unit, see Table 1).
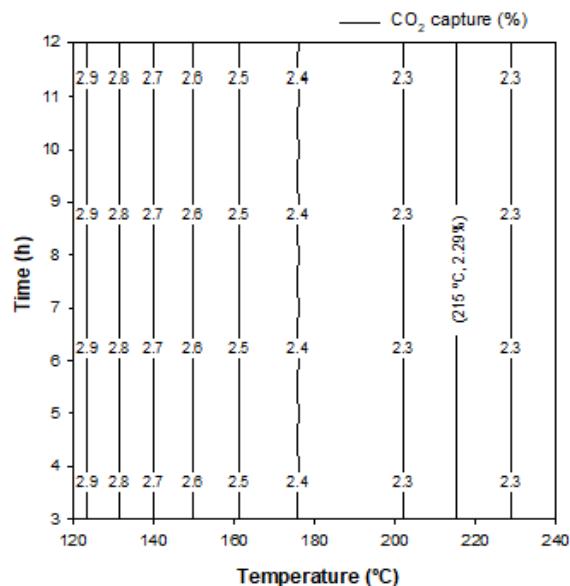

Figure 2. Response surface and contour plots for CO_2 capture capacity under flue gas conditions of the hydrochar derived activated carbons as a function of the HTC temperature and dwell time.

Sample	Experiment	Initial bed conditions	CO_2 sorption capacity (mmol g^{-1})	H_2O sorption capacity (mmol g^{-1})
RN2	Cycles	Fresh bed without complete regeneration in cycles	0.52	0.53
	Breakthrough curves	Fresh bed	0.62	1.92
		H_2O pretreatment	0.47	2.09
RN2K	Cycles	Fresh bed without complete regeneration in cycles	0.41	0.53
	Breakthrough curves	Fresh bed	0.49	4.09
		H_2O pretreatment	1.92	7.09

Table 1. CO_2 and H_2O sorption capacities of activated carbons in humid conditions at 50 °C and atmospheric pressure (14 kPa CO_2, 2 kPa H_2O, N_2 balance)

However, it was demonstrated that, independently of the H_2O concentration in the feed gas, a constant relative humidity of 20% in the RN2K bed (H_2O pretreatment case) promoted the carbonation reaction and boosted the CO_2 sorption capacity up to approximately 2 mmol/g at 50 °C and 14 kPa of CO_2.

Conclusions

The ability of activated carbon to adsorb CO_2 under post-combustion capture conditions is mainly ascribed to its microporosity. However, CO_2 uptake is reduced in humid environments due to the co-adsorption of water vapour. The present PhD

dissertation addressed this issue and focused on the adsorption of water vapour on biomass-based activated carbons and on the strategies available for reducing water uptake by means of surface chemistry modification. It was found that all of the evaluated post-treatments reduced to some extent the water uptake at low pressures but only amine impregnation succeeded under conditions close to saturation.

Likewise, the production of biomass-based activated carbons has been optimised and their potential for CO_2 adsorption under humid conditions maximised by combining different experimental procedures including the design of experiments with the Response Surface Methodology and modelling methods. Analysis of the equilibrium of adsorption together with the dynamic performance of beds of adsorbent (i.e., breakthrough curves and sorption-desorption cycles) provided data to support the great potential of the biomass-based adsorbents produced in this study to capture CO_2 under post-combustion conditions.

The CO_2 capture performance of coffee-based activated carbons was optimised and enhanced by hydrothermal carbonisation followed by activation with CO_2. The results achieved are more far-reaching than those reported in the patent ES2526259. On the other hand, under a constant relative humidity of 20%, a bed of a biomass carbon doped with potassium carbonate achieved a CO_2 uptake of up to 2 mmol g^{-1} at 50 ºC and 14 kPa CO_2. This result was accompanied by an outstanding volumetric CO_2 uptake.

Related Publications

[1] Querejeta, N.; Plaza, M.G.; Rubiera, F.; Pevida, C. Water Vapor Adsorption on Biomass Based Carbons under Post-Combustion CO_2 Capture Conditions: Effect of Post-Treatment. *Materials* **2016**, *9*, 359, DOI: 10.3390/ma9050359.

[2] Querejeta, N.; Gil, M. V.; Rubiera, F.; Pevida, C. Sustainable coffee-based CO_2 adsorbents: toward a greener production via hydrothermal carbonization. *Greenhouse Gases: Science and Technology* **2018**, *8*, 309–323, DOI: 10.1002/ghg.1740.

[3] Querejeta, N.; Rubiera, F.; Pevida, C. Enhanced capacity to CO_2 sorption in humid conditions with a K-doped biocarbon. *Journal of Energy Chemistry* **2018**, *34*, 208–219, DOI: 10.1016/j.jechem.2018.09.023.

Full thesis can be downloaded from *https://digital.csic.es/handle/10261/180199*