Design of cyclic adsorption processes for CO_2 capture in a waste management facility

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Objectives and Novelty

This Ph.D. thesis focused on the reduction of CO_2 emissions in a solid waste management facility as part of the transition to a green economy. A low-temperature adsorption technology using biomass-based adsorbents has been assessed for the separation of CO_2 in the two main gaseous streams produced in the generation of energy from waste. On the one hand, waste incineration produces heat and/or electricity; however, it also generates large amounts of CO_2. On the other hand, anaerobic digestion is an alternative route for treating the organic fraction of waste. Biogas from this process is an important renewable source of methane, but the presence of CO_2 reduces its energy content. Therefore, its separation is of paramount importance.

The study includes both the preparation of the adsorbent material and its dynamic evaluation in a fixed bed under dry and wet conditions, as well as the design and optimization of the adsorption process based on experimental and simulation results employing the software Aspen Adsorption™.

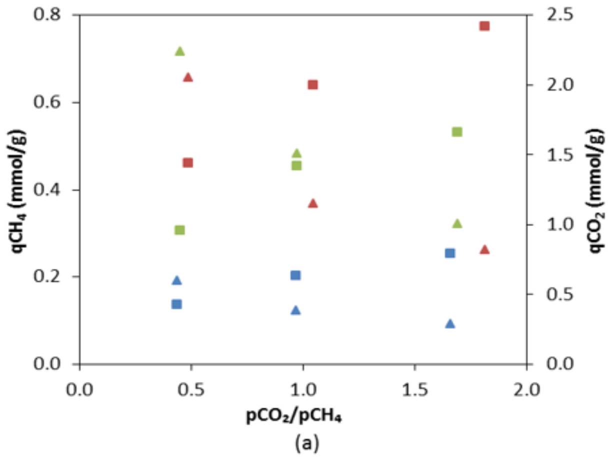
Results

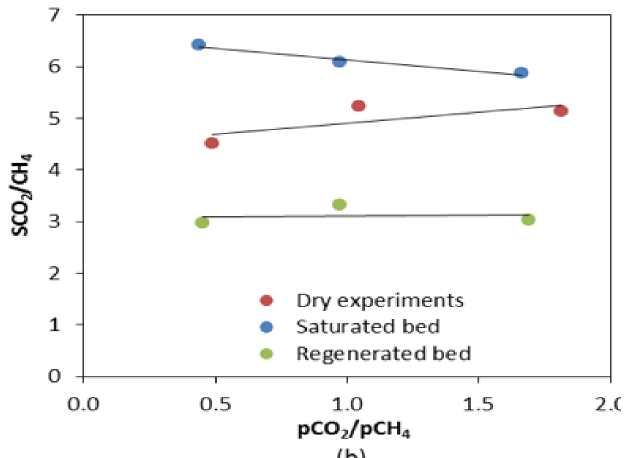
The first step was the preparation and characterization of the adsorbent material. The production of activated carbons from low-cost biomass precursors by physical activation with CO_2 in a single step was proposed. Pellets obtained from pine sawdust and its mixture with coal tar pitch, prepared under the conditions identified as optimal, have suitable properties for its use as CO_2 adsorbents. Sample IH3 (pine sawdust pellets activated with CO_2 at 800 °C, 1 h) presented a higher adsorption capacity on a mass basis, due to its greater textural development, and a better kinetic behaviour. Whereas IH2 (adsorbent prepared from mixtures of pine sawdust and coal tar pitch by an oxidation pretreatment for 1 hour at 300 °C and activated with CO_2 at 800 °C for 2 h) showed a very high carbon yield and higher mechanical strength. Both adsorbents had a greater affinity for CO_2 than for CH_4 and N_2.

In addition, the potential use of various species of microalgae as precursors was explored. *Chlorella* and *Spirulina* were evaluated both as freeze-dried microalgae and in fresh paste form, while *Acutodesmus Obliquus* and *Coelastrella sp.* were studied only as a paste. Activated carbons were produced using the selected species of microalgae as well as mixtures of pine sawdust and microalgae. Two different preparation routes were compared: with and without hydrothermal carbonization pretreatment prior to activation with CO_2. All samples were conformed into pellets before activation. Significant differences in terms of CO_2 adsorption capacity, carbon yield and pellet density were obtained among the species studied. Microalgae-pine sawdust blends showed an increase in the CO_2 adsorption capacities, even higher than that expected according to the additive rule. The hydrothermal carbonization process did not improve the adsorption capacity of the materials but a positive densification effect was observed.

In a second phase, the performance of the adsorbents under dynamic conditions was tested in a fixed-bed unit over consecutive adsorption−desorption cycles. For this purpose, the adsorbents IH3 and IH2 were selected. The maximum CO_2 capture capacities (breakthrough curves) were determined in both CO_2/N_2 and CO_2/CH_4 binary mixtures at different pressure and temperature conditions. Since both gaseous streams, incineration flue gas and biogas, contain significant amounts of water vapour, the effect of its co-adsorption with the other gas components was evaluated.

Dynamic adsorption experiments feeding binary CO_2/CH_4 mixtures at 30 °C and different pressures showed that IH3 reached the maximum CO_2 adsorption capacity under dry conditions at 1000 kPa; however, the highest CO_2/CH_4 selectivity factor was obtained at atmospheric pressure. In a wet biogas stream, the presence of pre-adsorbed water vapour reduced the adsorption capacity of CO_2 and CH_4 but favoured the adsorbent selectivity towards the CO_2 (see Figure 1). Optimal operating conditions were identified to carry out biogas purification under wet conditions: atmospheric pressure and $pCO_2/pCH_4 \approx 0.5$.





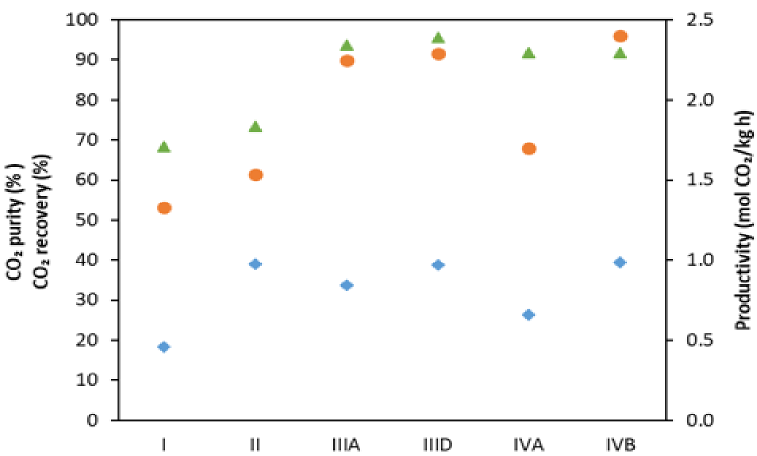
As it is observed in Table 1, the evaluation under representative conditions of the incineration flue gases showed that the most unfavourable conditions for CO_2 adsorption are: a completely saturated water vapour bed at the beginning of the cycle and a wet gas feed with a high relative humidity, here exemplified by a ternary $CO_2/N_2/H_2O$ mixture at 30 °C. However, in conditions of low relative humidity (i.e., 50 °C), the CO_2 capture capacity of these activated carbons was not affected by the presence of water vapour and nitrogen.

Figure 1. (a) CH_4 (triangles) and CO_2 (squares) adsorption capacities at atmospheric pressure vs CO_2/CH_4 partial pressure ratio in the feed gas, (b) Selectivity factor vs CO_2/CH_4 partial pressure ratio: comparison between dry (red circles) and wet biogas experiments over a regenerated (green circles) and a saturated bed (blue circles) at atmospheric pressure.

		High relative humidity (60%)		Low relative humidity (22%)	
Experiment	Adsorbent	q_{CO_2} (mmol/g)	t_b,CO2 (min)	q_{CO_2} (mmol/g)	t_b,CO2 (min)
Fresh bed	IH3	0.72	4.9	0.40	3.1
	IH2	0.59	3.0	0.33	1.9
Saturated bed	IH3	0.29	2.1	0.41	3.1
	IH2	0.22	1.0	0.35	1.8

Table 1. CO_2 adsorption capacities (q_{CO_2}) and breakthrough times (t_b) when feeding a ternary $N_2/CO_2/H_2O$ mixture at low and high relative humidity to the IH3 and IH2 beds.

Finally, the design and optimization of cyclic processes of adsorption and desorption were conducted. Different cyclic configurations in conditions close to the real ones encountered in an industrial process, i.e., avoiding saturation of the bed, were evaluated for its application in a waste incineration plant. This required the analysis and evaluation of multiple parameters: the number of columns, the configuration of steps, the operating pressure and temperature, regeneration strategies, etc. These factors, together with the properties of the adsorbent, determine the productivity of the process and the degree of purity and recovery of the product (CO_2 in this case). The results obtained for the VSA (Vacuum Swing Adsorption) and VTSA (combined Vacuum and Temperature Swing Adsorption) cycle configurations are gathered in Figure 2.



I = 2 beds, 3 steps (pressurization, adsorption, desorption)

II = 3 beds, 4 steps (pressurization, adsorption, rinse with CO_2, desorption)

IIIA = 3 beds, 5 steps (pressurization, adsorption, rinse with CO_2, desorption, purge with N_2)

IIID = VTSA configuration equivalent to IIIA

IVA = 2 beds, 5 steps

IVB = 4 beds, 5 steps

Figure 2. Characteristic parameters determined for the different VSA and VTSA configurations analysed at an adsorption temperature of 50 °C.

For the optimal configuration, CO_2 could be concentrated from a feed gas stream with 8 vol.% of CO_2 (N_2 balance) at 50 °C to 39.4%. CO_2 recovery ranged from 53.1 to 96.0% and N_2 concentration in the decarbonised stream from 96.4 to 99.4%, depending on the cycle configuration used. Afterwards, the experimental data were employed to validate a numerical model, based on mass, momentum and energy balances, developed for the CO_2 adsorption-desorption process in the fixed-bed lab unit. For this purpose, the commercial software Aspen Adsorption™ was used. Moreover, simulations of the adsorption process were carried out with alternative configurations that could not be evaluated due to experimental limitations of the lab unit. When carrying out evacuation and purge with N_2 stages counter-currently, a notable improvement in product recovery, but not in average CO_2 purity was achieved. On the other hand, the introduction of pressure equalization stages and the decrease of the purge flow with N_2 slightly increased the CO_2 purity.

Conclusions

Activated carbons prepared from pellets of pine sawdust, and mixtures with coal tar pitch, are mainly microporous and have suitable properties for application as CO_2 adsorbents. The production of activated carbons from microalgae is feasible if combined with the addition of a lignocellulosic biomass. The sample prepared with a mixture of Spirulina paste and pine sawdust, activated directly with CO_2, was the most promising in terms of CO_2 adsorption capacity: 4 wt.% at 50 °C and a partial pressure of CO_2 of 10.5 kPa.

Dynamic fixed-bed evaluation of the adsorbents showed that maximum CO_2 adsorption capacity is reached under dry conditions. The presence of pre-adsorbed water vapour in the bed leads to lower CO_2 adsorption capacity under high relative humidity conditions. However, in the case of biogas, it favours the selectivity of the adsorbent towards the CO_2 instead of CH_4. Therefore, it is possible to find an operational window to carry out the biogas purification under wet conditions. In the incineration case, the CO_2 capture performance of the evaluated adsorbents was not affected by the presence of water vapour at low relative humidity, so ideally a cycle design would keep the moisture content low considering the slow kinetics of water vapour adsorption.

The design of vacuum cyclic adsorption processes for incineration flue gases in a single fixed-bed device showed that, with relatively simple configurations consisting of a maximum of 4 beds, CO_2 recoveries above 95% were achieved and CO_2 was enriched from 8% in the feed to 40% in the product. The numerical model developed for the adsorption process adequately reproduced the experimental results.

Related Publications

[1] Durán I, Rubiera F, Pevida C. Vacuum swing CO_2 adsorption cycles in Waste-to-Energy plants. Chemical Engineering Journal 2020; 382; doi: 10.1016/j.cej.2019.122841.

[2] Durán I, Álvarez-Gutiérrez N, Rubiera F, Pevida C. Biogas purification by means of adsorption on pine sawdust-based activated carbon: Impact of water vapor. Chemical Engineering Journal 2018; 353:197–207; doi: 10.1016/j.cej.2018.07.100.

[3] Durán I, Rubiera F, Pevida C. Microalgae: Potential precursors of CO_2 adsorbents. Journal of CO_2 Utilization 2018; 26:454–464; doi: 10.1016/j.jcou.2018.06.001.

[4] Durán I, Rubiera F, Pevida C. Separation of CO_2 in a solid waste management incineration facility using activated carbon derived from pine sawdust. Energies 2017; 10(6):827–846; doi: 10.3390/en10060827.

[5] Plaza MG, Durán I, Rubiera F, Pevida C. CO_2 adsorbent pellets produced from pine sawdust: Effect of coal tar pitch addition. Applied Energy 2015; 144:182–192; doi: 10.1016/j.apenergy.2014.12.090.

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