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A low-cost way to reduce greenhouse effects

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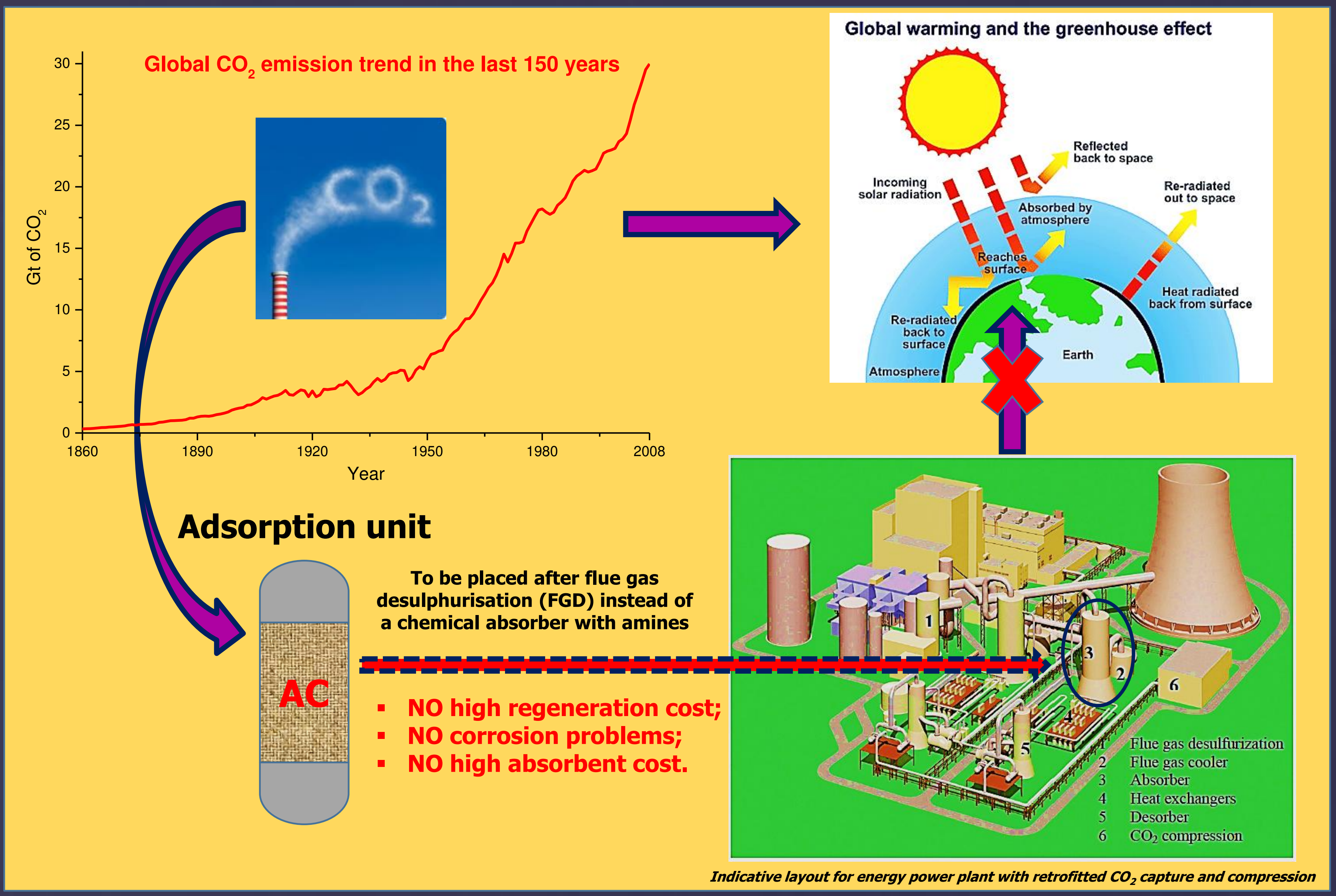
Abstract Oak wood precursor was used for preparing low-cost CO_2 sorbents. Adsorption is proposed as a cheaper alternative to chemical absorption, which is uneconomical, thus reducing the cost associated with the capture step. The raw material has been carbonised either by pyrolysis or by a hydrothermal carbonisation (HTC). Resulting biochars were then activated using CO_2 . Initial chars and their activated counterparts were characterised by SEM imaging and N_2 sorption measurements at 77 K. A significant rise in the BET surface area, total pore volume and micropore volume (textural parameters) occurred for all of the pristine chars after the activation process. Fast CO_2 sorption kinetics (saturation reached in 3 mins.) and CO_2 uptakes of up to ca. 6 wt. % have been measured by thermogravimetric analysis (TGA) at 35 ºC and 1 atm. The activated carbons (ACs) thus synthesised showed competitive performances compared to a commercial AC standard. Although the sorbents' performances decreased at higher temperatures, they were easily regenerated after the capture stage.

Introduction



Adsorption unit

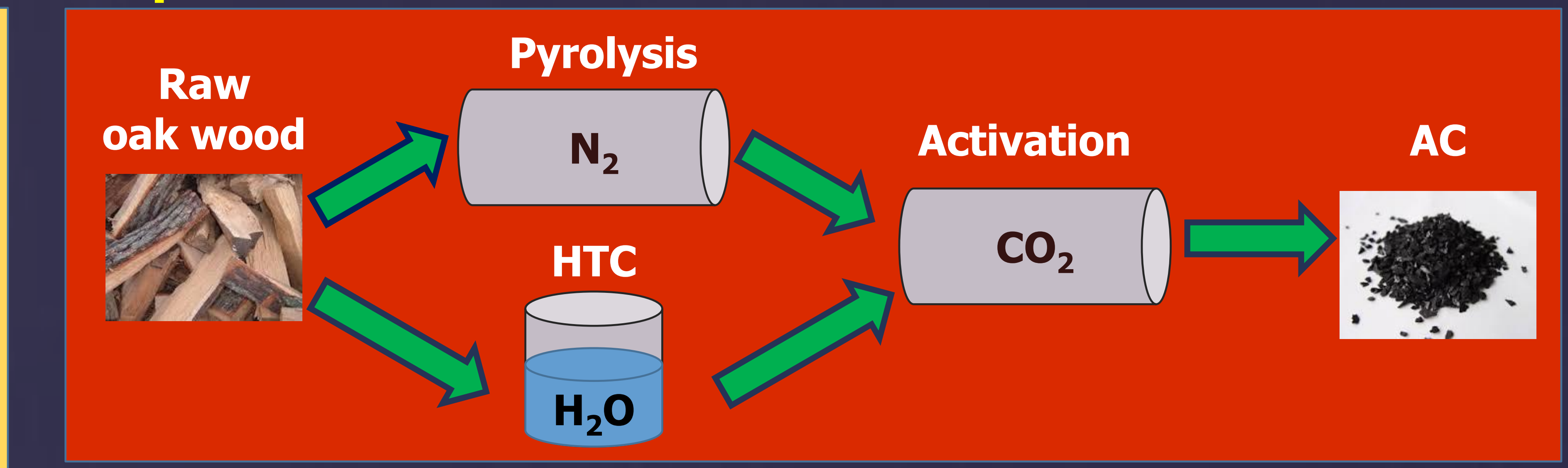
To be placed after flue gas desulphurisation (FGD) instead of a chemical absorber with amines

- **NO high regeneration cost;**
- **NO corrosion problems;**
- **NO high absorbent cost.**

1 Flue gas desulfurization
2 Flue gas cooler
3 Absorber
4 Heat exchangers
5 Desorber
6 CO_2 compression

Indicative layout for energy power plant with retrofitted CO_2 capture and compression

Experimental



Raw biomass was subjected either to a dry pyrolysis, in a horizontal tube furnace at 650 or 800 ºC under N_2, or to hydrothermal carbonisation (HTC) carried out in deionised water at 250 ºC in stainless steel autoclaves. Carbonisation products (named OW650, OW800 and OW250, respectively) were then heat-treated under CO_2. N_2 adsorption isotherms at 77 K for both pristine chars and oak wood-based ACs (referred to as OW250A, OW650A and OW800A) were measured using a Quantachrome Autosorb 1C gas sorption analyser. The materials' surface morphology has been examined by using a LEO 1530 (Field Emission Gun) High Resolution SEM. CO_2 uptakes for the ACs produced, and a commercial carbon (denoted as GAC) included for comparison purposes, were measured by using TGA both at 35 ºC (isothermal test) and with temperature increasing from 35 to 100 ºC (temperature-programmed test). Finally, the atmosphere was switched to N_2 and the temperature was increased to 120 ºC to regenerate the samples.

Results and discussion

From Figs. 1a-1b it is possible to see the effect of the activation on the pore structure of the biochars. The ACs' isotherms tend to be closer to type I and their pore size distributions are narrower with peaks centred over ca. 0.5 nm. As observed from Fig. 2, moderately higher surface areas and micropore volumes were found for ACs derived from pyrolysis products (OW650 and OW800).

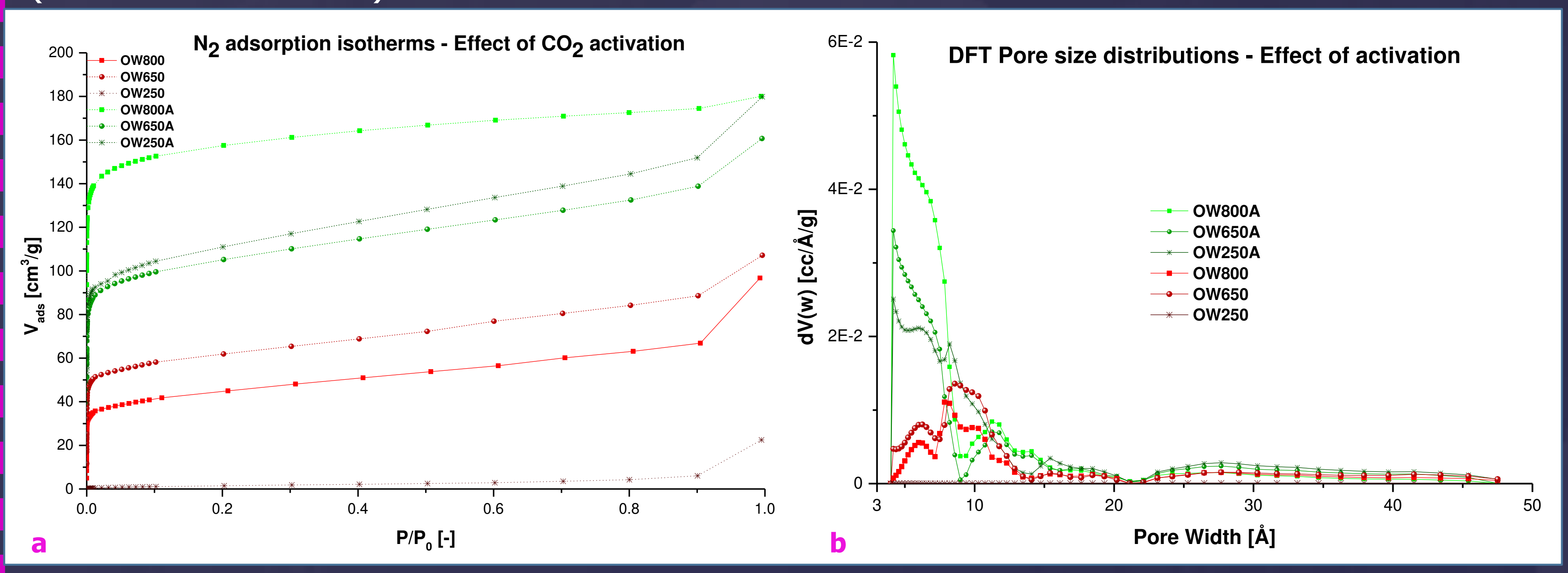


Figure 1. (a) N_2 adsorption isotherms and (b) DFT pore size distributions for biochars and ACs

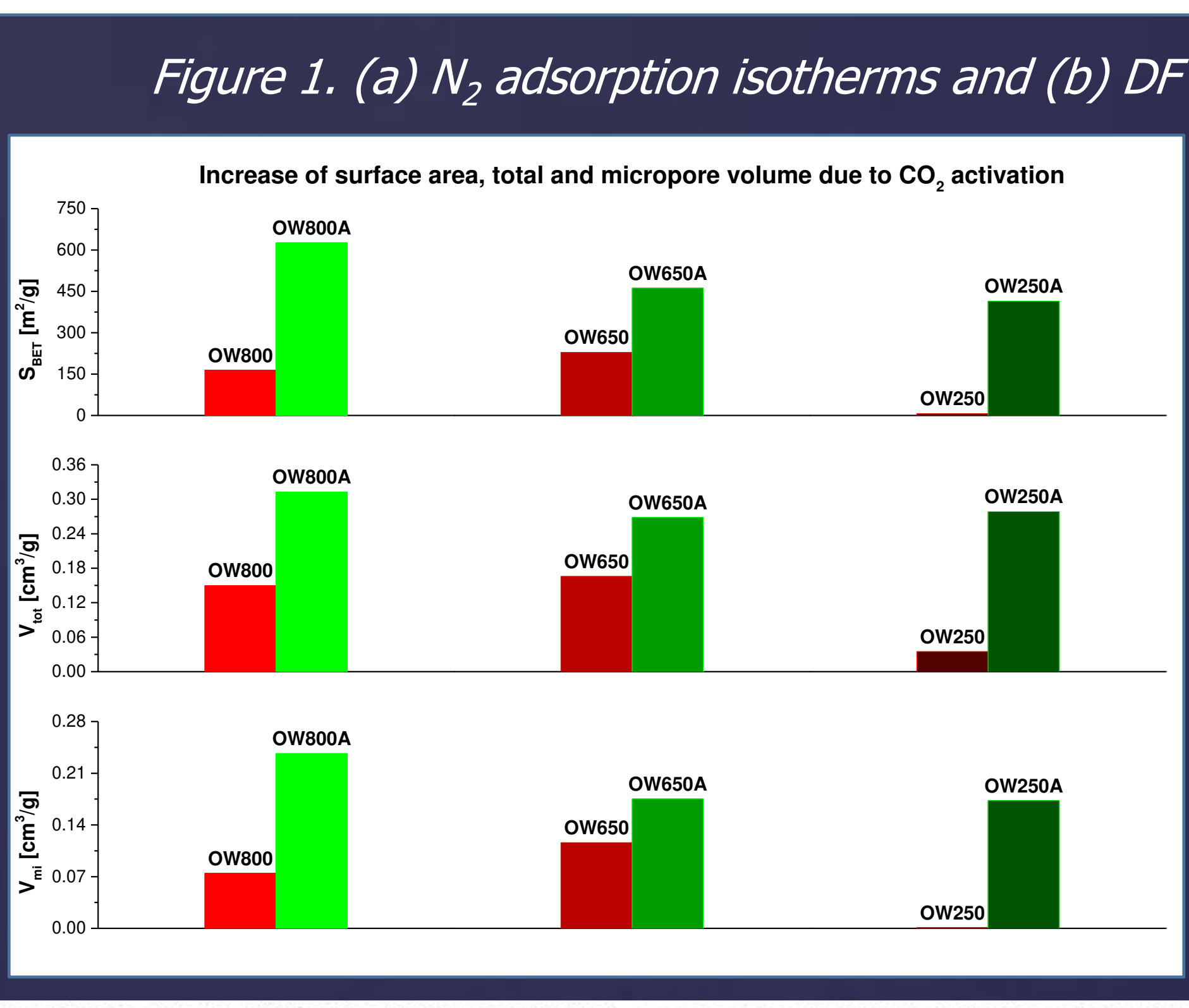


Figure 2. Enhancement of textural parameters after CO_2 activation of all the biochars (OW800, OW650, OW250).

On the other hand, the most dramatic development of texture occurred for the activated carbon derived from the hydrothermally carbonised sample (OW250), whose surface area increased nearly 100 fold compared to the starting biochars' figure.

Textural characterisation results are corroborated by SEM images (see Fig. 3).

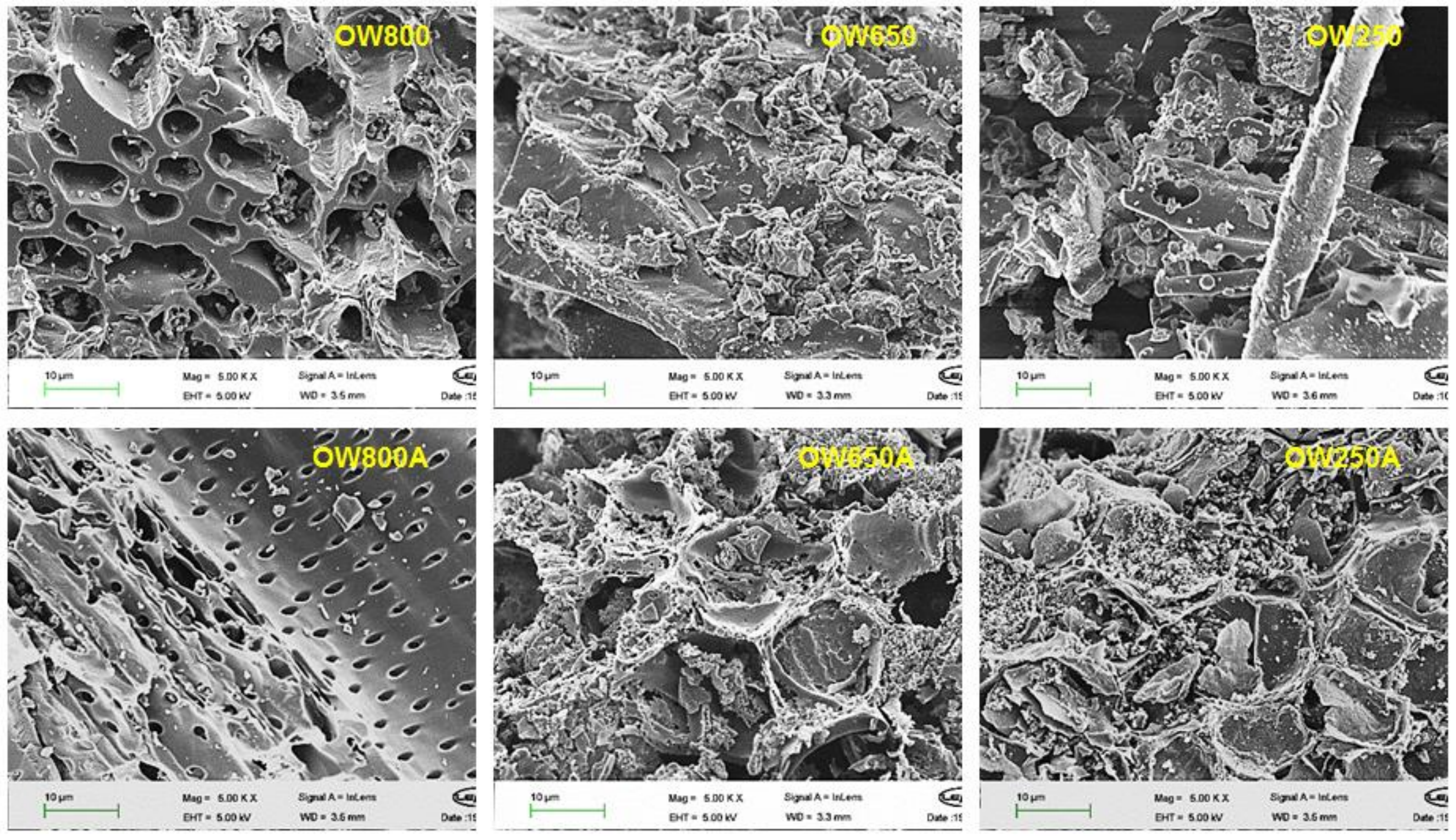


Figure 3. SEM micrographs at 5000x for biochars & ACs.

Indeed, these clearly show development of a structure that is more porous due to the activation procedure. (Microporosity is too small to see of course)

Moreover, as seen in Fig. 3, the regular distribution of mesopores identified for OW800A confirms its more porous structure compared to OW650 and OW250 which have larger pores that are also occupied by inorganic particles.

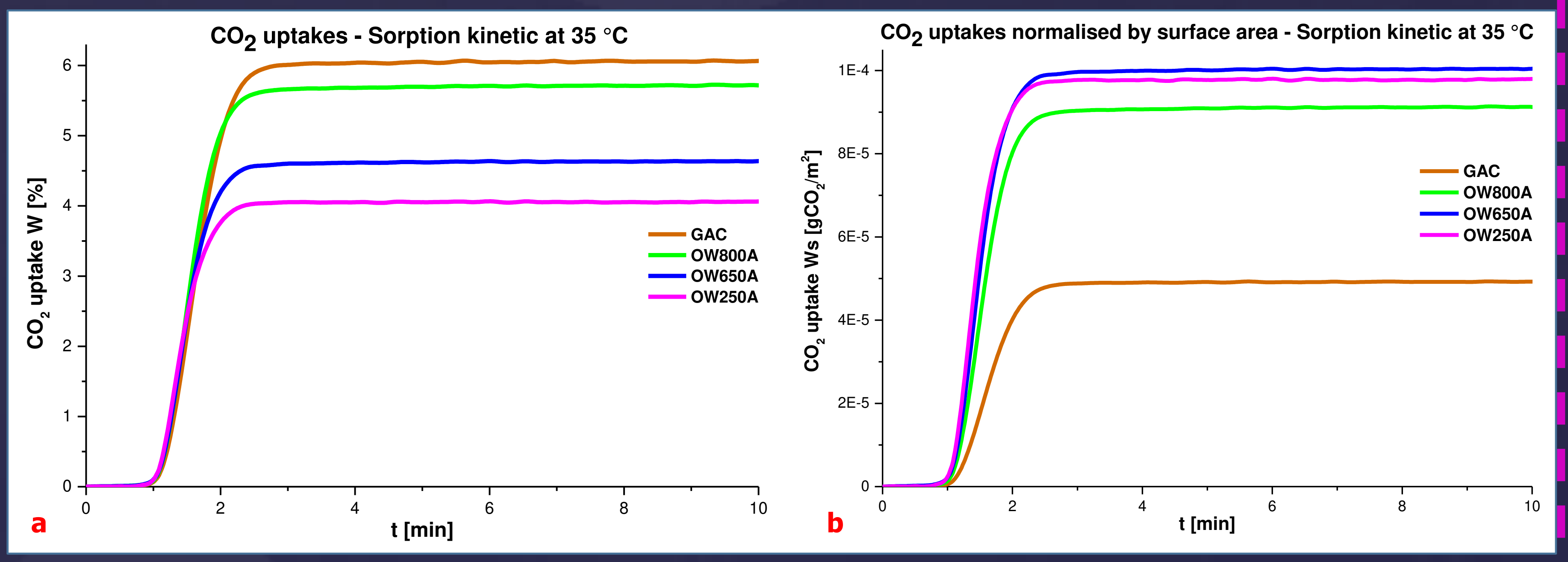


Figure 4. (a) Isothermal CO_2 uptakes at 35 °C expressed as percentage of weight increase of the fresh sorbent (W) and (b) normalised by surface area (Ws)

From the CO_2 uptake measurements carried out under isothermal conditions (35 °C) over 30 mins. as reported in Fig. 4a, it is observed that all the sorbents tested have fast sorption kinetics towards CO_2 uptake. Indeed, saturation is always reached within 3 mins. The maximum uptake is ca. wt. 6% which is comparable or even higher than values reported in some studies and achieved under similar conditions [1-2] but it is still a long way from the best performances (ca. 21%) reported in the literature [3].

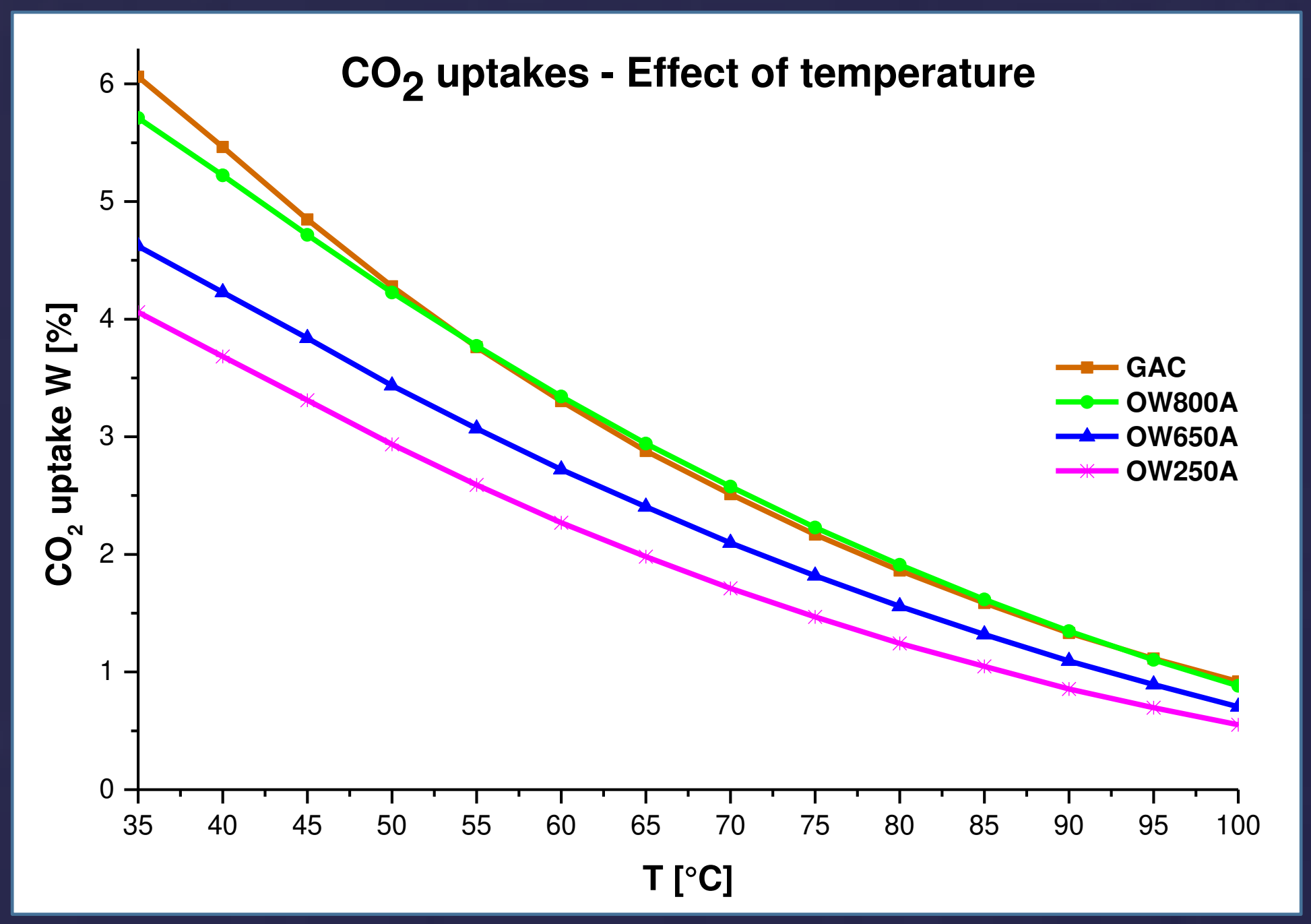


Figure 5. Effect of temperature on CO_2 uptakes

Nevertheless, as evidenced by Fig. 4b, where uptakes are normalised to the samples' surface area, it is interesting to note that, despite the far larger surface area possessed by the commercial activated carbon (GAC's figure is twice that of OW800A), the wood-based ACs adsorbed much more CO_2 per unit of surface area, which might suggest that the latter possess greater affinity towards CO_2 due to, e.g., basic functional groups.

Fig. 5 shows that, for all of the samples tested, sorption capacities decrease with increasing temperature as physisorption is an exothermic process. Nevertheless, This reduction occurs only gradually over the analysis temperature range, thus indicating a relatively strong adsorption potential binding CO_2 to the pore structure of the materials even at more severe temperatures. Finally, as shown by Fig.6, all the sorbents were easily regenerated in less than 2 mins. under N_2 at 120 °C.

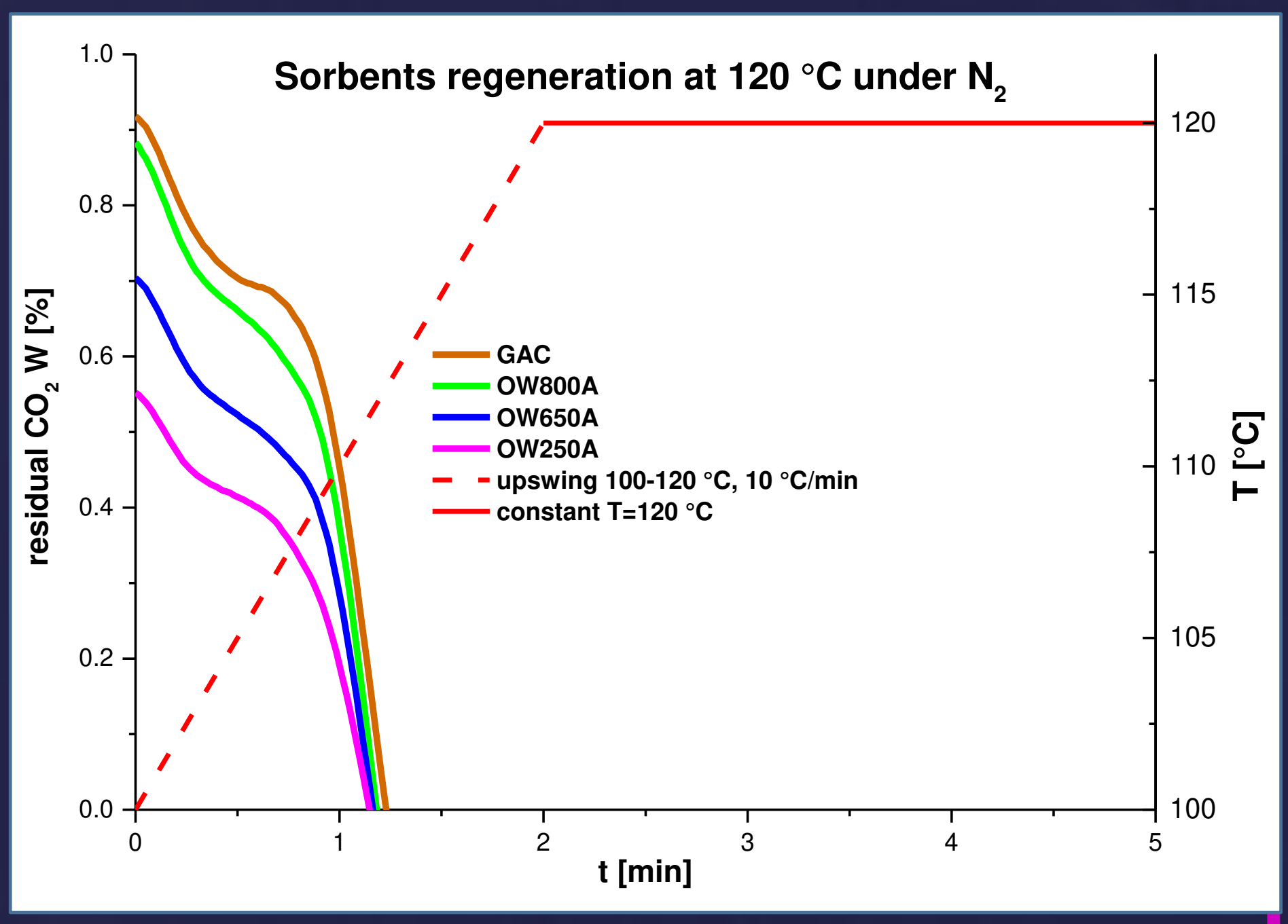


Figure 6. Sorbent regeneration at 120 °C under N_2

Conclusions

Carbonisation products derived from a low-cost biomass (oak wood) were successfully activated. Significant improvements to their porous texture were obtained – in particular for the hydrochar whose surface area was increased by around 100 fold. This demonstrates that the innovative HTC process, which operates at milder temperature conditions compared to those of traditional pyrolysis, can lead to hydrochar-derived ACs with surface areas comparable to those attained for sorbents derived from pyrolysed biochars. Overall, promising CO_2 sorbents have been produced starting from a low-cost feedstock, which showed similar uptakes to those achieved by commercial ACs (around 6 wt. %) and fast sorption rates. In addition, all of the materials were completely regenerated at 120 °C in ca. 2 mins. Future work will focus on applying an appropriate chemical modification of these carbons in an attempt to maximise their performances in terms of CO_2 uptakes under post-combustion conditions since they show promise as a viable alternative to costly chemical absorption of CO_2.

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[3] Sevilla et al. (2012). High-performance CO_2 sorbents from algae. RSC Advances, 2(33), 12792