PREPARATION OF ACTIVATED HYDROCHARS AS ADSORBENTS

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INTRODUCTION

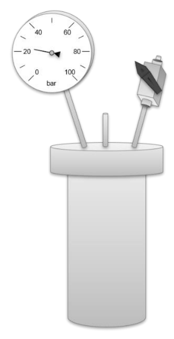
Hydrothermal carbonization (HTC), has recently been studied in depth as an environmentally friendly alternative to the usual thermochemical conversion methods of biomass to produce biochar (i.e., pyrolysis, gasification and torrefaction). The main advantages of the HTC process are its lower energy consumption, fewer gaseous emissions and higher solids yield. However, the chars produced via HTC (hydrochars) have small surface area and poor porosity, which limits their scope of application as adsorbents. On that basis, chemical and physical activation were successfully used to improve the porous structure of hydrochars. Thus, by modifying the morphology and chemical surface, activated hydrochars can be used as adsorbents of pollutants from aqueous and gaseous environments with positive results.

OBJECTIVE

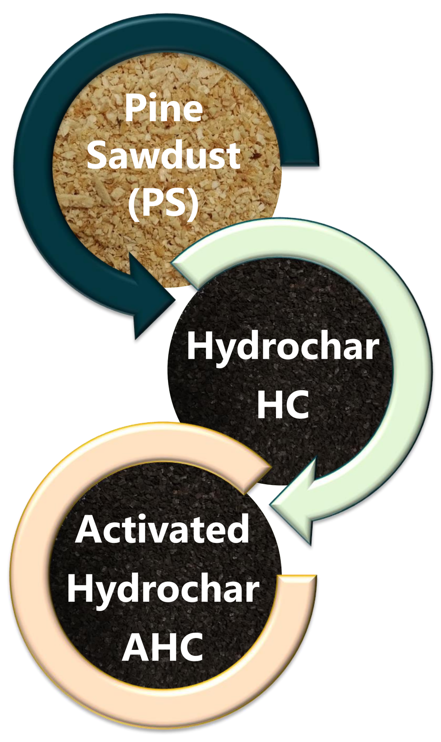
The main objective of this work was to produce and characterize activated hydrochars to determine the optimal conditions to use them in different environmental scenarios.

EXPERIMENTAL

HYDROTHERMAL CARBONIZATION



- Biomass: 1-3 mm
- Biomass / water 1:5
- Initial pH: 5
- Temperature: 220 °C
- Residence time: 4h

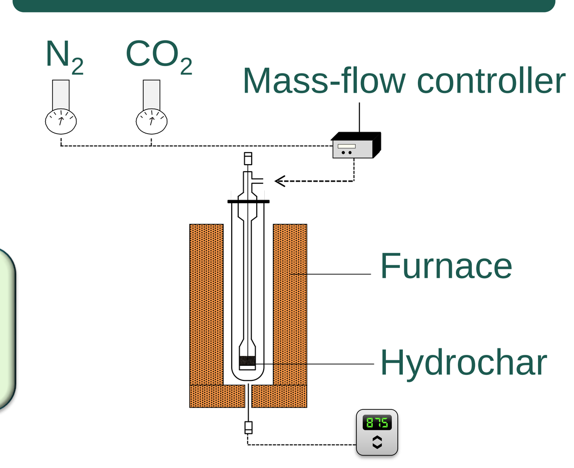


Activation type

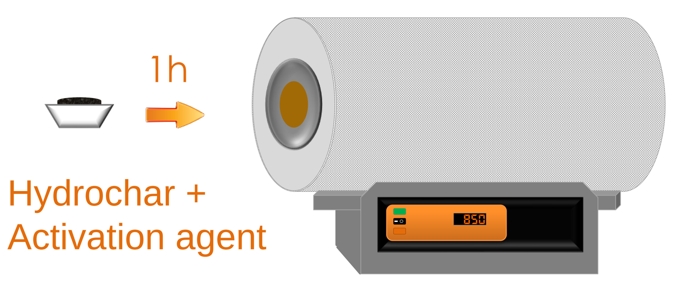
HYDROCHAR ACTIVATION

Activation conditions

PHYSICAL ACTIVATION



CHEMICAL ACTIVATION



Activated HC	AHC-CO_2	AHC-KH	AHC-KH+AC	AHC-KH+M
Activation agent	CO_2	$KHCO_3$	$KHCO_3$+NH_4Cl	$KHCO_3$+Melamine
Temperature	875 ºC	850 ºC	850 ºC	800 ºC

AHCs CHARACTERIZATION

- Ultimate analysis
- N_2 adsorption isotherms
- XPS
- CO_2 ADSORPTION MEASUREMENTS

RESULTS AND DISCUSSION

Ultimate Analysis

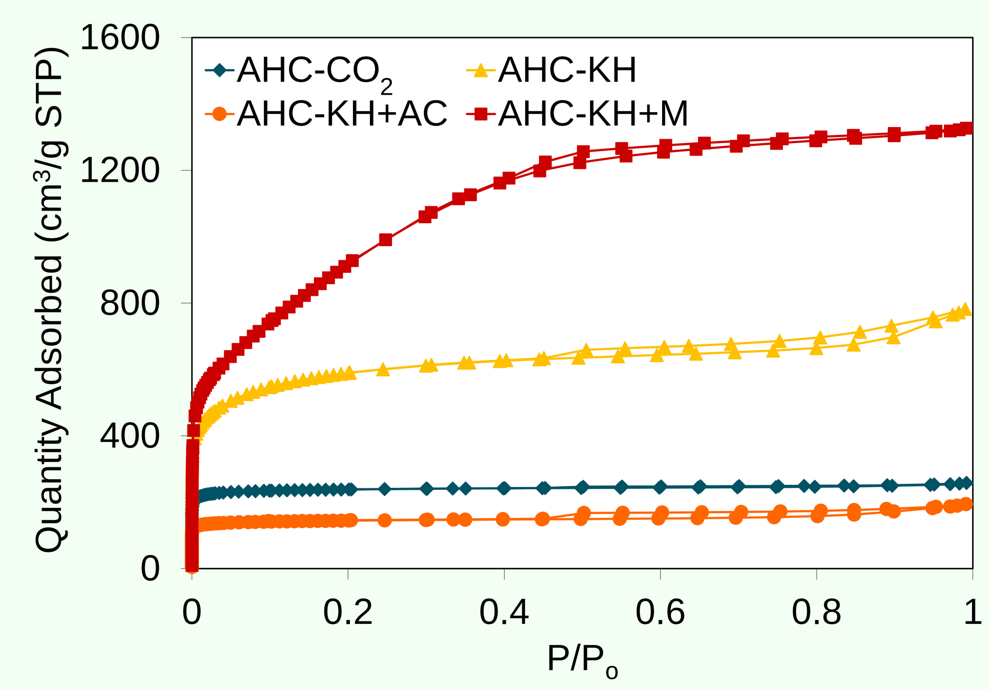
	Chemical composition (wt.%, db[a])				XPS (wt.%)		
	C	H	N	O	C	N	O
PS	52.0	6.3	0.3	41.2	--	--	--
HC	71.1	5.0	0.3	23.5[b]	--	--	--
AHC-CO_2	96.9	0.4	1.0	1.7[b]	93.9	--	6.1
AHC-KH	93.0	0.2	1.3	5.5[b]	93.1	--	6.9
AHC-KH+AC	91.6	0.6	1.3	6.5[b]	89.9	--	10.1
AHC-KH+M	93.5	0.3	1.9	4.3[b]	93.9	0.8	5.4

[a]Dry basis. [b]By difference.

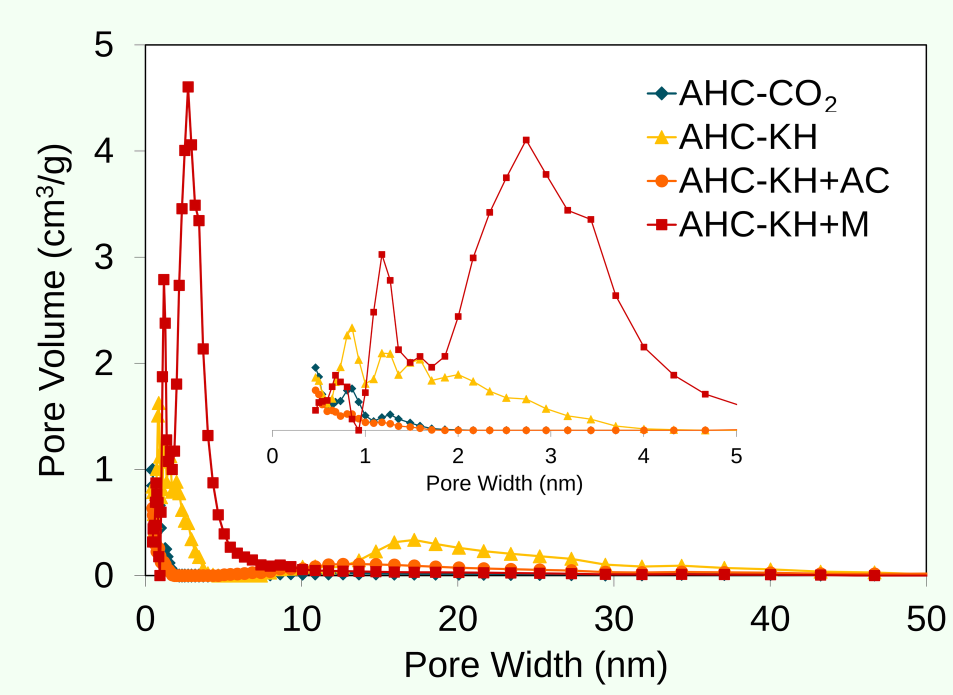
- The HTC treatment of pine sawdust led to an increase in C content and a decrease in H and O content. After activation this variations are more noticeable.
- XPS analysis showed higher O content for all activated hydrochars, indicating that the surface is more oxidized than the bulk.

N_2 Adsorption Isotherms And Pore Size Distribution Of Hydrochars

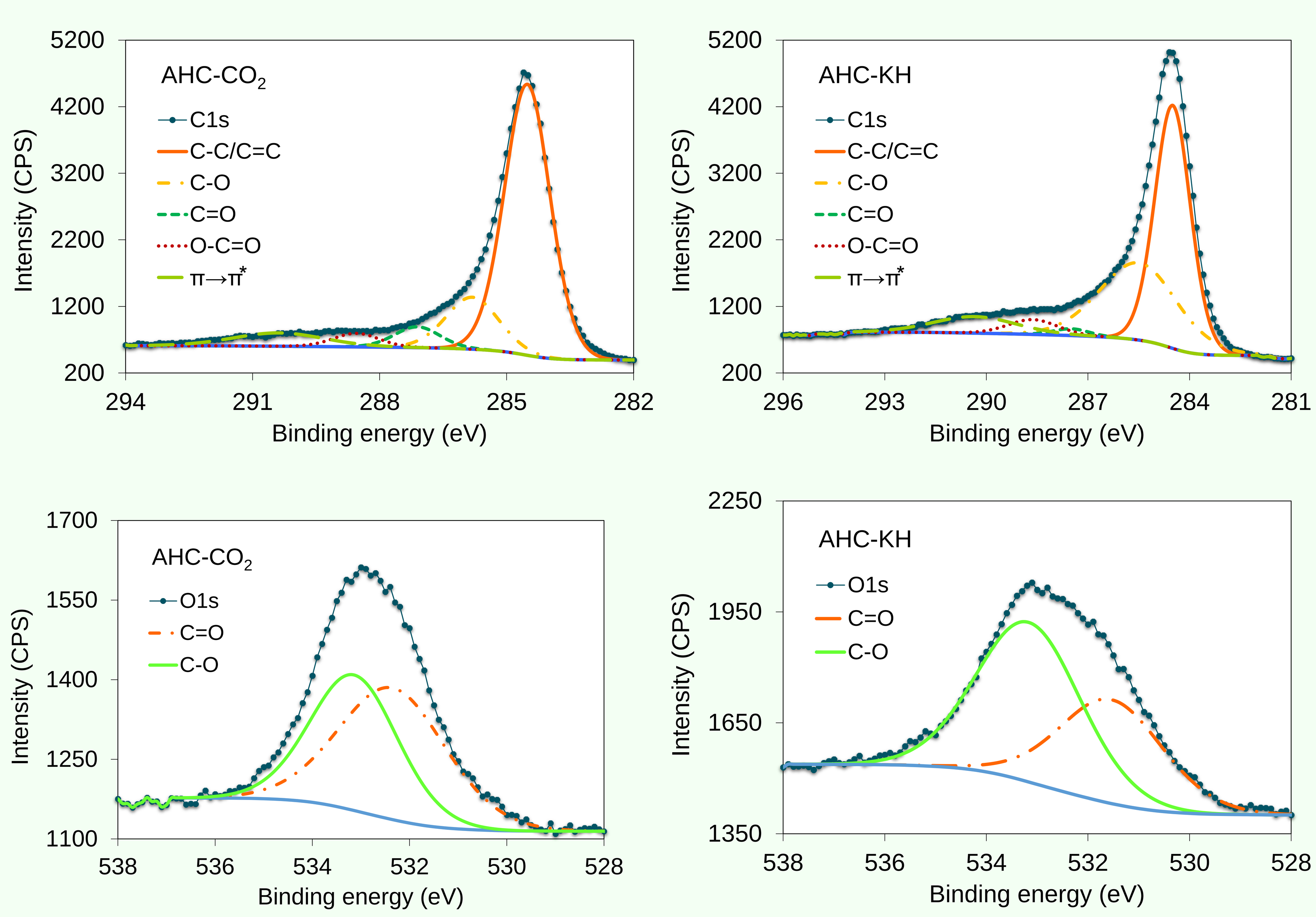
The N_2 adsorption isotherms of AHCs are of Type I, indicating microporous characteristics. The specific surface area (S_{BET}) and the corresponding total pore volume (V_T) ranges between 552–3276 m²/g and 0.29–2.04 cm³/g, respectively.



AHCs are mainly composed of micropores and contained a considerable number of small-scale mesopores (2 ~ 5 nm).
Physically activated HCs and AHC-KH+AC do not exhibit any pores of size >2 nm. AHC-KH-M is dominated by pores centered at ca. 2–5 nm.



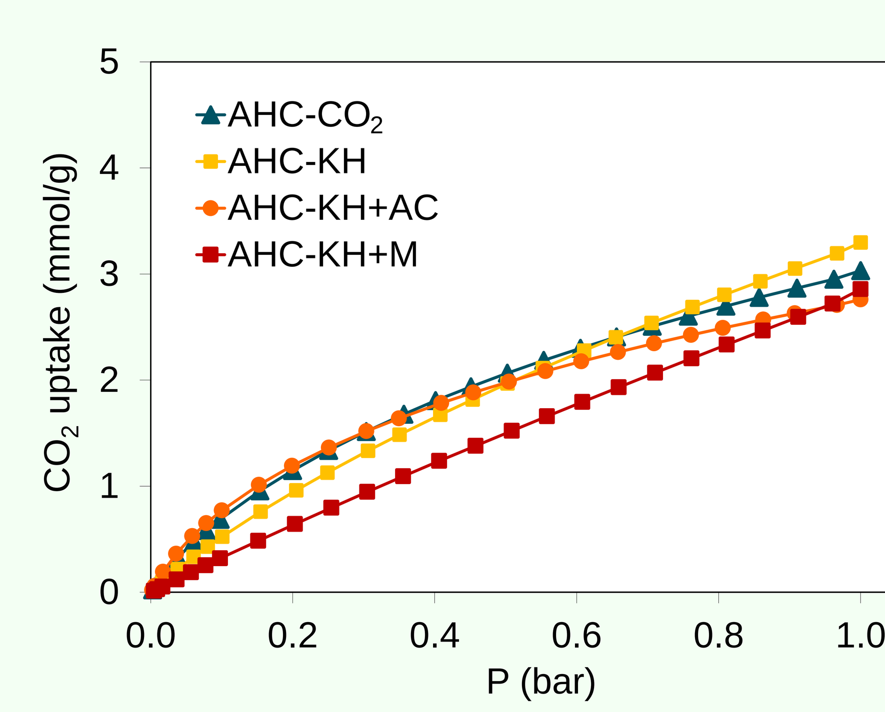
X-ray Photoelectron Spectroscopy



The graphitic carbon (C-C / C=C) is the main component for all hydrochars. The O-containing groups are mainly in form of ether, epoxy or hydroxyl (O-C, O-C-O and C-OH), carbonyl (C=O) and carboxyl (O-C=O).

The O1s spectra show peaks corresponding to carbonyl-carboxyl (C=O and –O-C=O) and hydroxyl ether (C-O and C-O-C). Except AHC-CO_2 the rest of activated hydrochars show higher proportion of C-O groups.

CO_2 Adsorption Measurements



The CO_2 uptake measured at 25 °C ranges between 2.76 - 3.30 mmol/g. AHC-KH, the activated hydrochar with large number of narrow micropores (<1 nm), shows the highest CO_2 adsorption capacity.

CONCLUSIONS

- Activated hydrochars showed good CO_2 uptake at 1 bar. The hydrochar activated with $KHCO_3$ showed the largest CO_2 uptake (3.30 mmol/g).
- The addition of melamine led to high BET surface area material which, according to its PSD, may also be a potential adsorbent for liquid-phase applications, as in water pollutant removal.

ACKNOWLEDGEMENTS

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