Preparation of foamed and unfoamed geopolymer/NaX-zeolite/activated carbon composites for CO_2 adsorption

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WORKSHOP

Geopolymer for Environmental Remediation

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Introduction

- The current energy scenario is heavily dependent on **fossil fuels.**
- **Their combustion** is responsible of the **emissions of greenhouse gases** that produce permanent and **irreversible damage** to the climate system.

Carbon Capture, storage and utilization of greenhouse gases **(CCSU)**

Carbon capture and geological storage of greenhouse gases **(CCS)**

Current CO_2 capture technologies include:

The absorption

The adsorption

Emerging and crucial challenges:

- The improvements of the **CO_2 adsorption capacity** of materials
- Improvements in the **efficiency** of the adsorption and absorption processes

The absorption

Involves the bulk of a solid, liquid or gas. Atoms or molecules cross the surface and enter the volume of the material

Physical: a non-reactive process

Chemical: a chemical reaction takes place

Chemical absorption of amine scrubbing

Used in industrial settings such as power plants. It is: **Expensive**, with high amounts of **waste**, equipment **corrosion**, **low efficiency, high energy consumption** during the regeneration process and flow problems caused by **viscosity**

The adsorption

Is a **surface process** (accumulation of a gas or liquid on a liquid or solid), defined as:

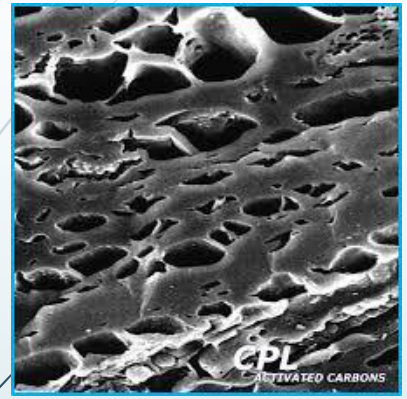
Physisorption (Van der Waals interactions) formation).

Chemisorption (Chemical bonds formation).

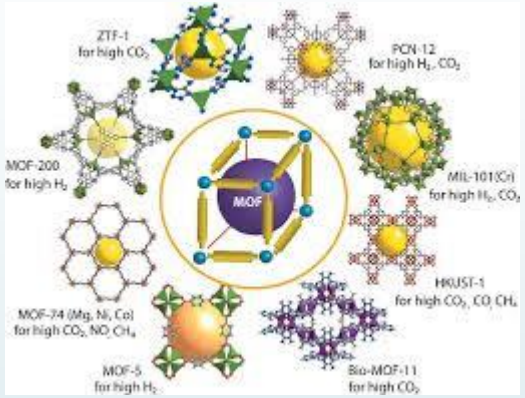
A **valid alternative** to conventional absorption with liquid solvents.
A **lower environmental impact**, **more straightforward and effortless operation and recovery of the adsorbent.**

CO_2 Adsorbents

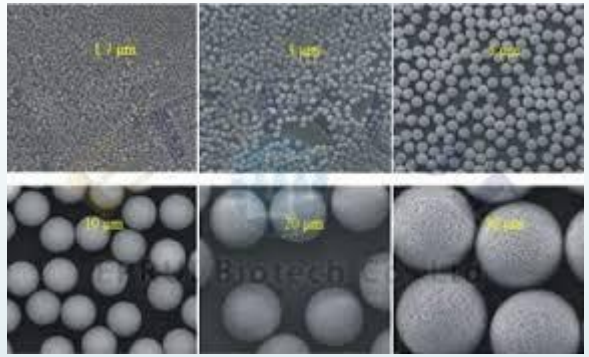
Activated Carbon



Metal-organic frameworks

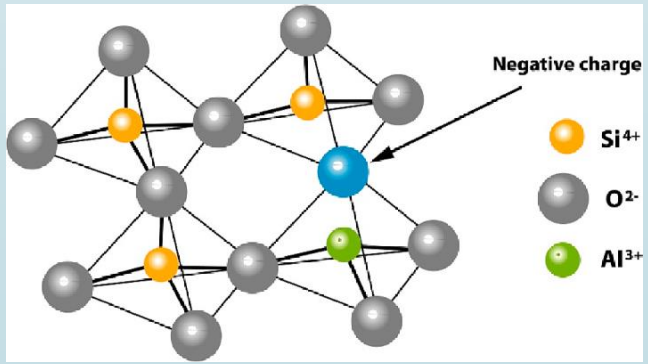


Silica gel



High fast kinetics, tailored pore structure, hydrophobic character, low energy for regeneration, low heat of adsorption and high stability

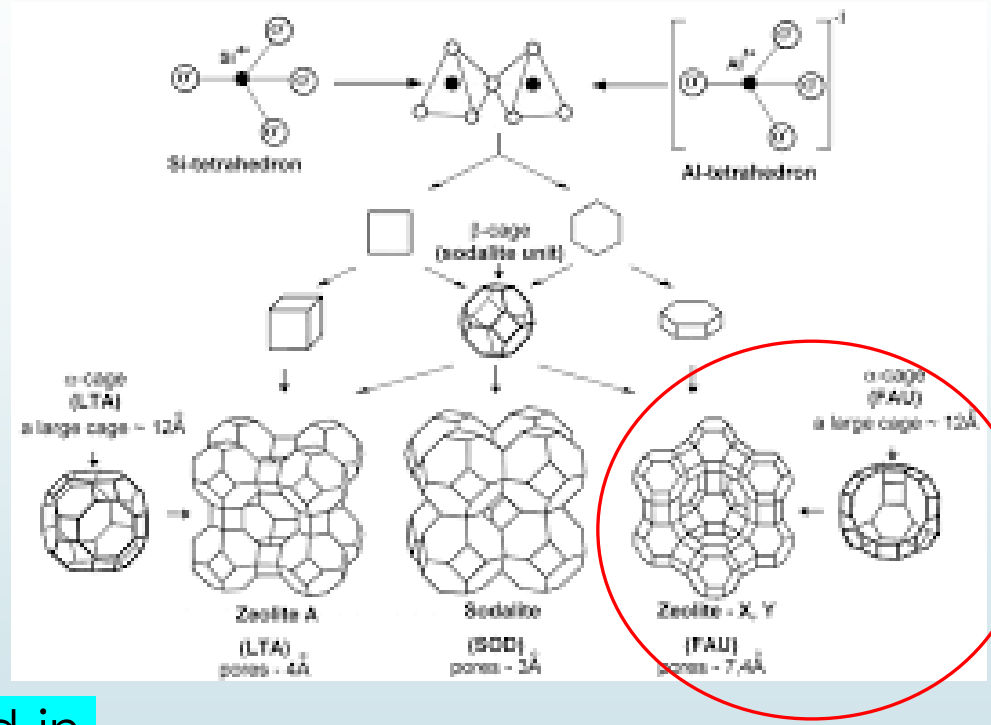
Zeolites



Zeolites are crystalline materials built up by several connected (TO4: T = Si or Al) tetrahedra creating a network of channels and cavities with well-defined pore size at the molecular level.

Na-13X CO_2 adsorbent

NaX zeolite is a benchmark material for CO_2 capture because its framework has a strong electric field that preferentially adsorbs molecules with large dipole and quadrupole moments such as CO_2



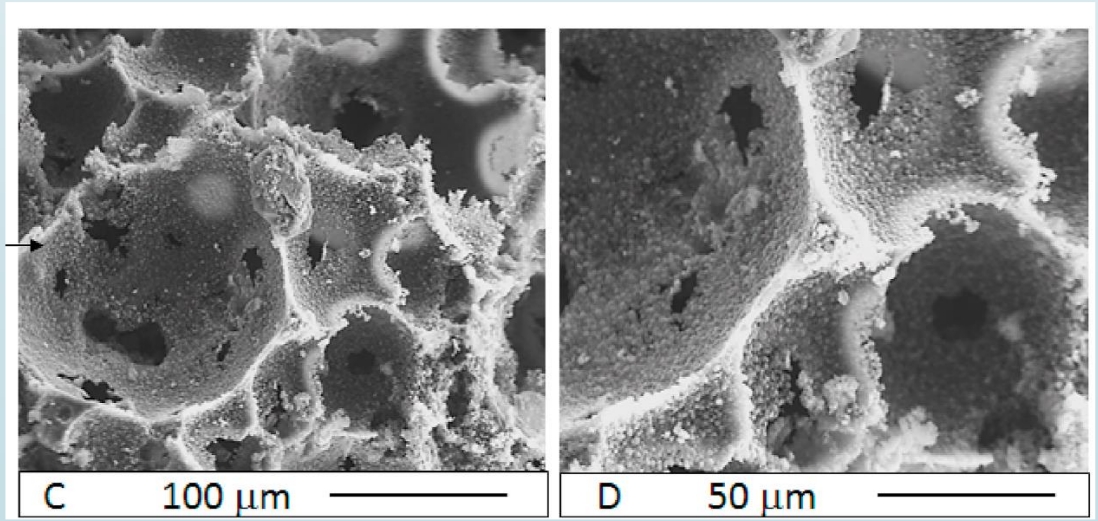
Zeolites cannot be used in powder form in industrial applications

Supporting or shaping them is required for:

- ❑ increasing their mechanical resistance
- ❑ Avoiding high-pressure drop and channeling

Present study

- Authors prepared different hybrid adsorbents via geopolymerization, followed by in situ NaX gel conversion, of a slurry obtained by mixing an activator solution, metakaolin and activated carbon.
- Foamed hybrid adsorbents were also prepared by adding a foaming agent and a surfactant to the slurry.
- The zeolite/activated carbon composites were investigated as their combination can result in less severe heat effects on the PSA performance due to lower heat of adsorption of CO_2 on activated carbons than zeolites.
- hierarchical micro/meso/macroporosity has been proposed to overcome the low mass transport coefficients and large pressure drops that characterize swing adsorption processes



Activated Carbon

Activated carbon (AC) was prepared from deoiled olive pomace waste ("Sansa esausta" (SE), locally produced) through carbonization followed by combined KOH and thermal activation.

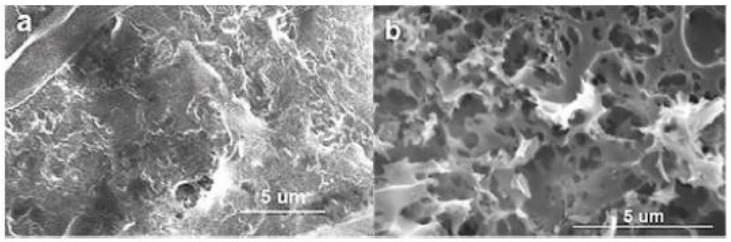


Fig. 2. Micrographs of: a) Deoiled olive pomace waste; b) Activated biochar.

5

Abarca, Candamano et al. 10.1051/e3sconf/202014802006

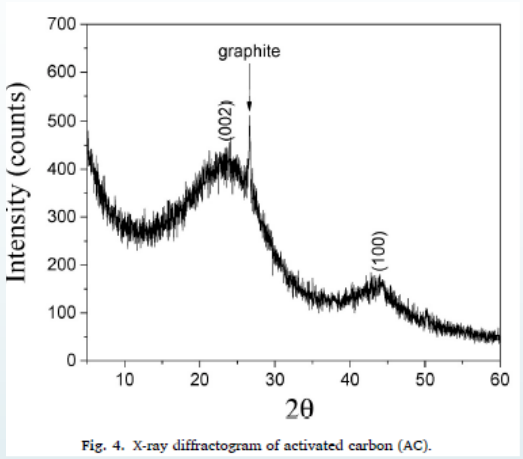


Fig. 4. X-ray diffractogram of activated carbon (AC).

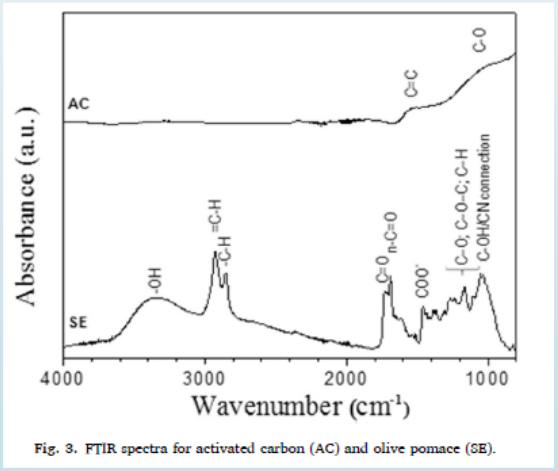
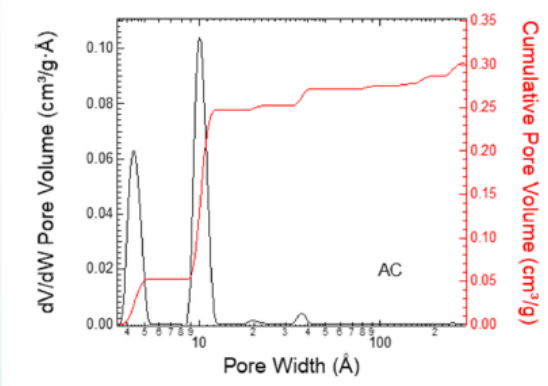


Fig. 3. FTIR spectra for activated carbon (AC) and olive pomace (SE).



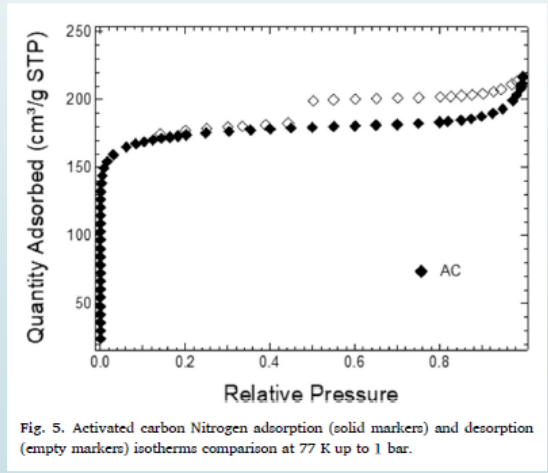
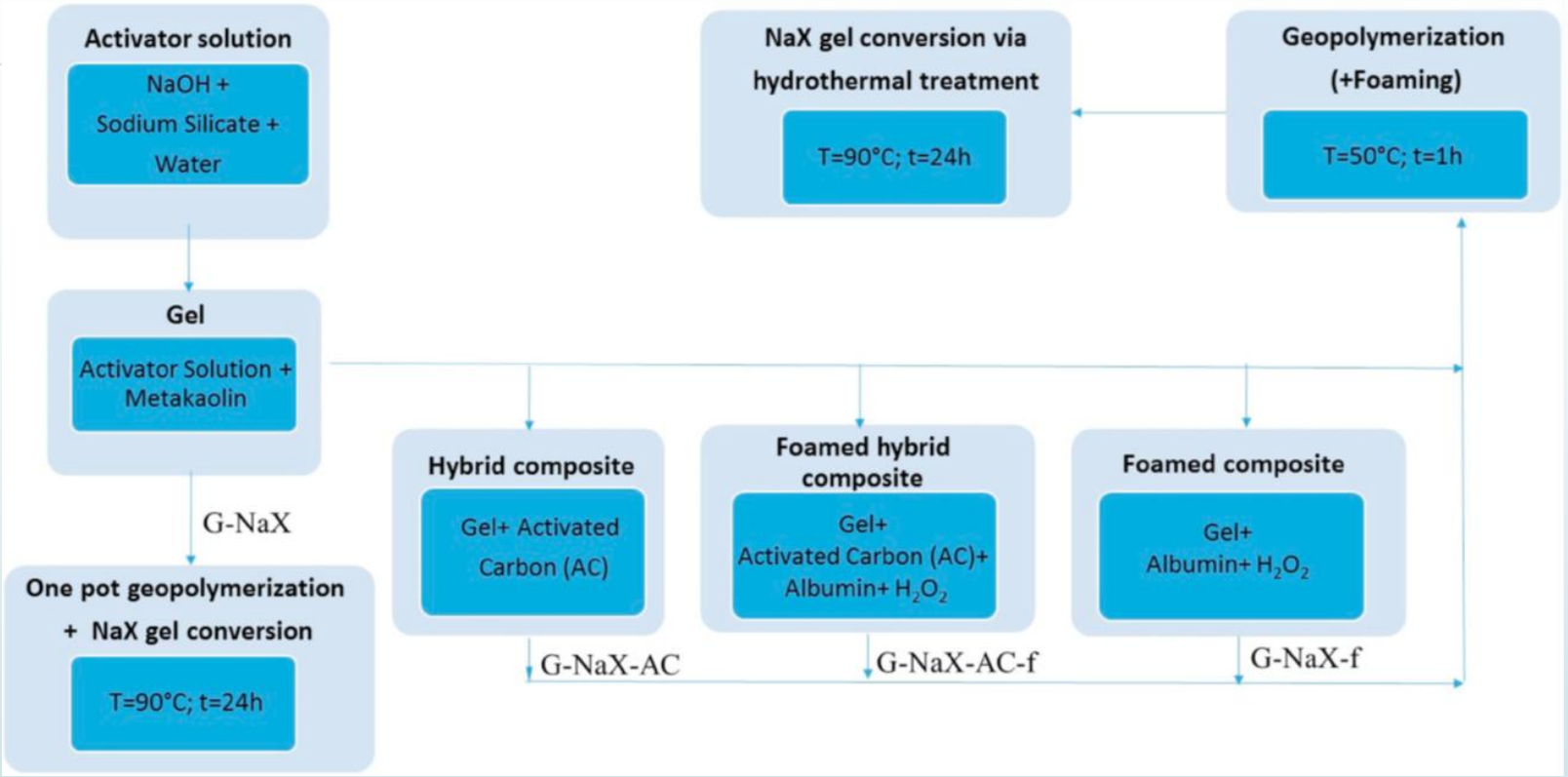


Fig. 5. Activated carbon Nitrogen adsorption (solid markers) and desorption (empty markers) isotherms comparison at 77 K up to 1 bar.

Structural parameters of the analyzed AC sample.

Sample	S_{BET} [m^2/g]	V_{mic} [cm^3/g]	V_{mes} [cm^3/g]	V_T [cm^3/g]
AC	528	0.250	0.052	0.302

Experimental

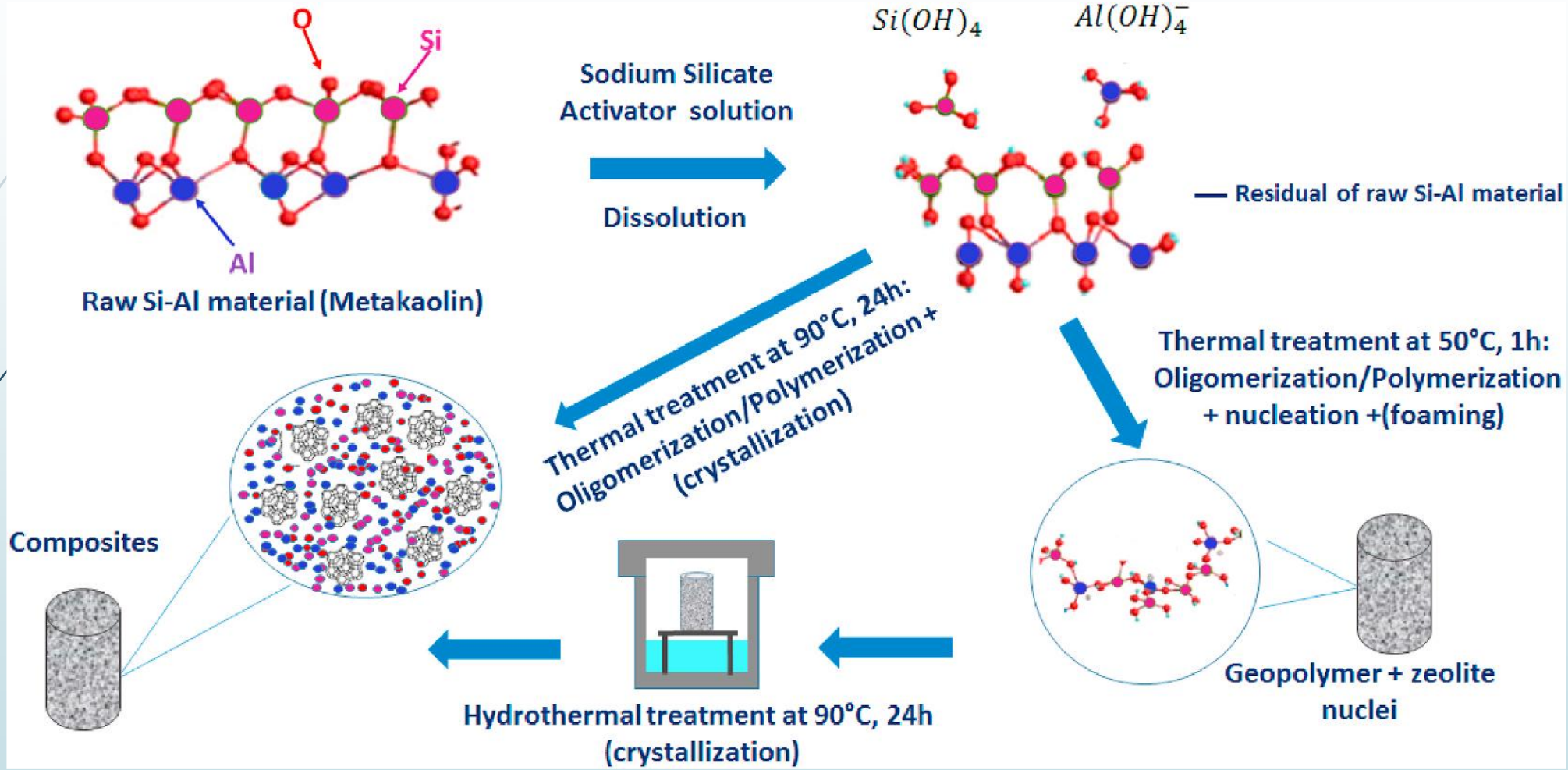


Composition of activator solution and samples.

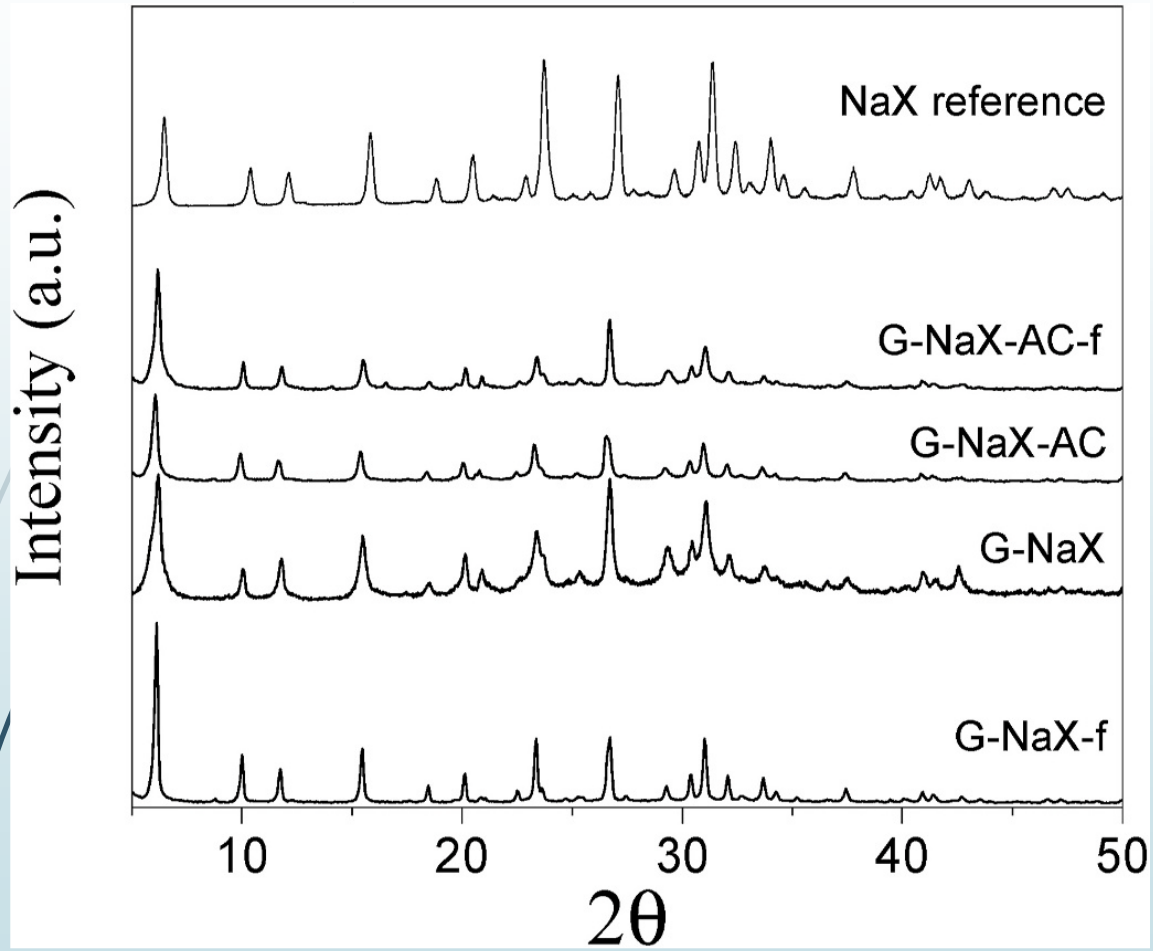
Sample	Activator Solution		Gel	Additives		
	SiO_2/Na_2O (Ms)	Na_2O/H_2O	Molar composition	H_2O_2 (wt%)[a]	AC (wt%)[a]	Albumin (wt%)[a]
G-NaX	0.63	0.108	$1.3Na_2O{\cdot}3SiO_2{\cdot}1Al_2O_3{\cdot}12H_2O$	0	0	0
G-NaX-f	0.63	0.108	$1.3Na_2O{\cdot}3SiO_2{\cdot}1Al_2O_3{\cdot}12H_2O$	3	0	1.7
G-NaX-AC	0.63	0.108	$1.3Na_2O{\cdot}3SiO_2{\cdot}1Al_2O_3{\cdot}12H_2O$	0	20	0
G-NaX-AC-f	0.63	0.108	$1.3Na_2O{\cdot}3SiO_2{\cdot}1Al_2O_3{\cdot}12H_2O$	3	20	1.7

[a] Weight percentage on metakaolin.

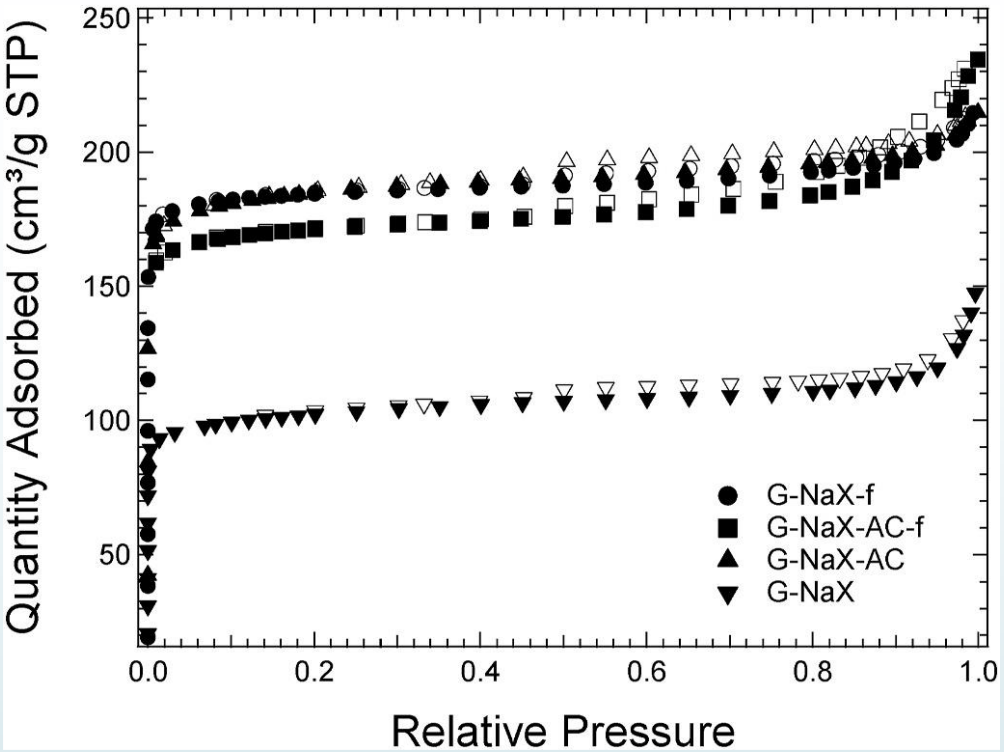
Overall reactions' scheme



Results



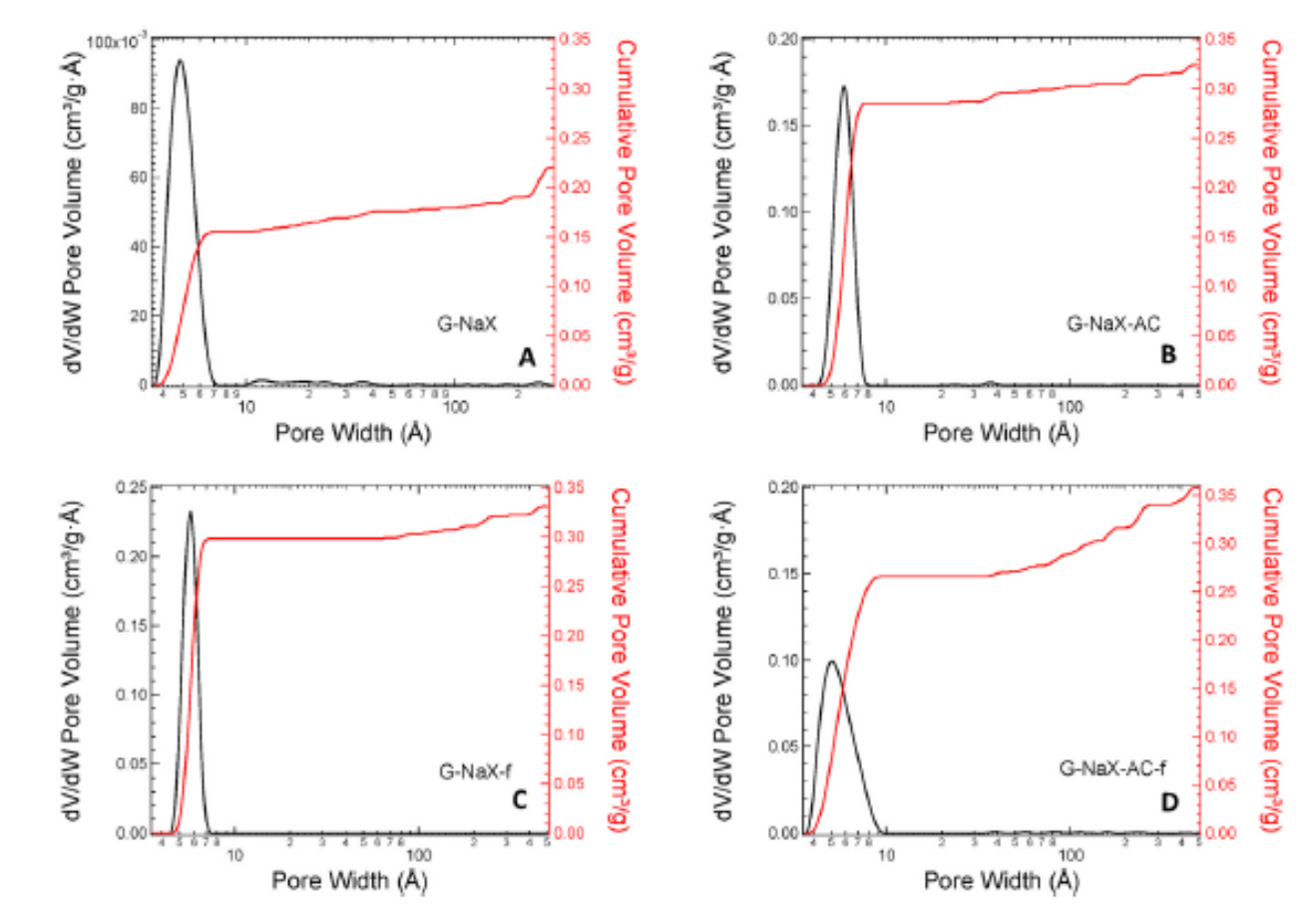
Candamano et al.10.1016/j.jclepro.2021.129843



Structural parameters and compressive strength of analyzed samples.

Sample	Skeletal Density [g/cm^3]	S_{BET} [m^2/g]	V_{mic} [cm^3/g]	V_{mes} [cm^3/g]	V_T [cm^3/g]	Compressive strength [MPa]
G-NaX-f	1.67 ± 0.04	752	0.298	0.033	0.331	1.0 ± 0.1
G-NaX-AC	1.98 ± 0.02	735	0.285	0.039	0.324	12.2 ± 0.5
G-NaX	2.26 ± 0.09	343	0.164	0.057	0.221	16.0 ± 0.7
G-NaX-AC-f	1.71 ± 0.04	693	0.266	0.092	0.358	1.0 ± 0.1

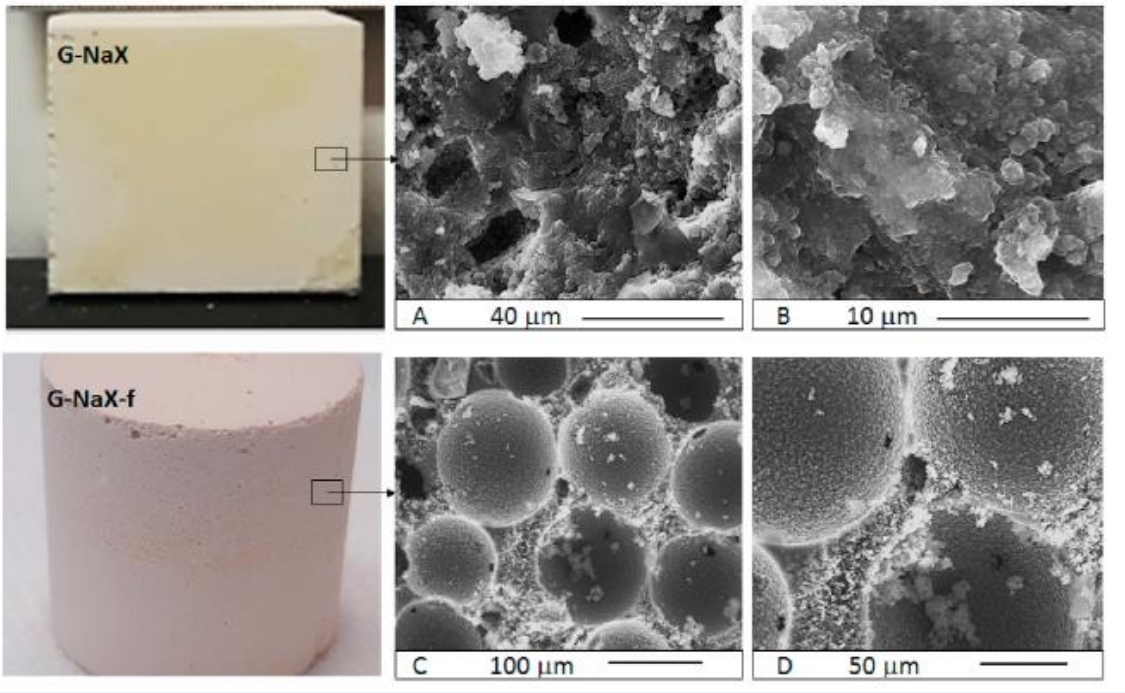
Results

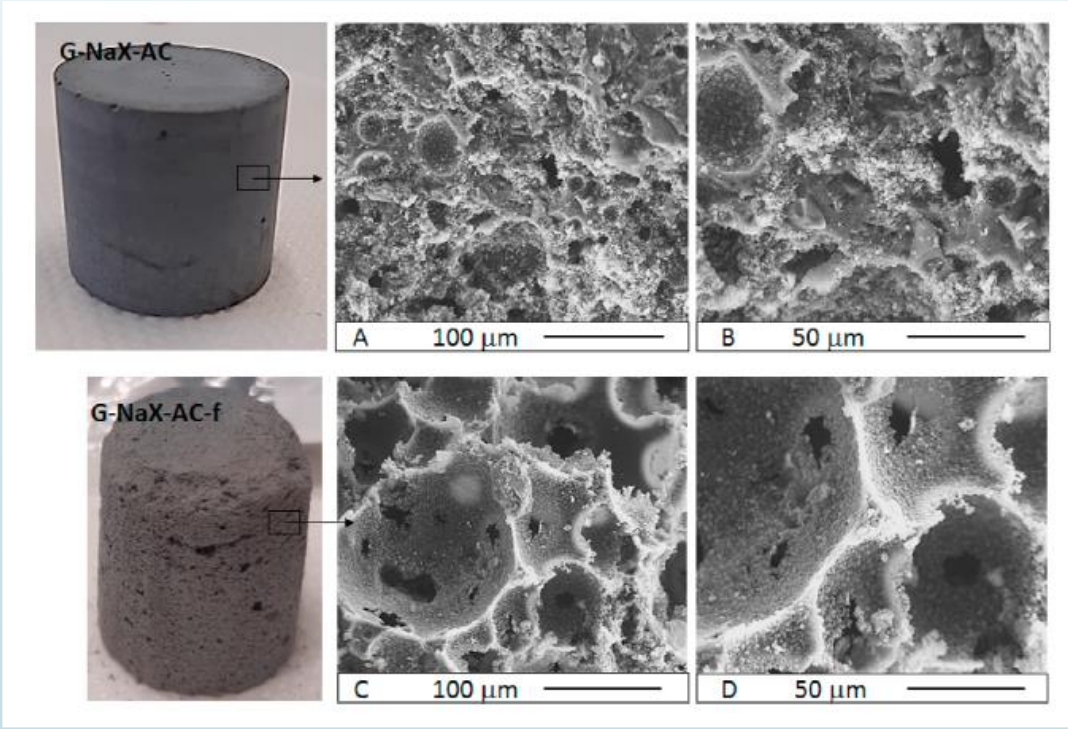


Pore size distributions (black) and cumulative pore volume (red) calculated from N_2 isotherms using the DFT heterogeneous surface model.

- All four samples have a microporous structure (<20 Å) with a prevalent ultramicro porosity (<7Å) and residual mesoporosity (>20 Å) contribution.
- An evident difference among the analyzed samples occurs for pores width more than 10Å.
- Only the G-NaX-AC-f sample shows a prevailing combination of ultra(<7 Å) and super micro (7–20 Å) pores, with a contribution of mesoporous greater than the other samples.

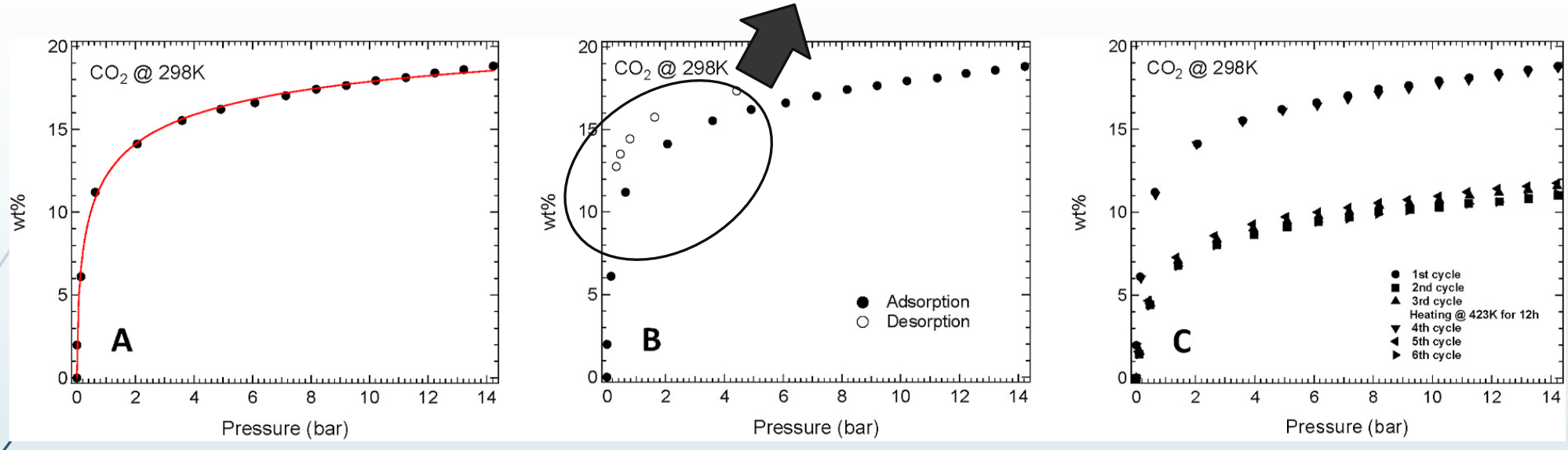
Microstructures





CO_2 adsorption

Hysteresis:strong adsorbent/adsorbate interaction



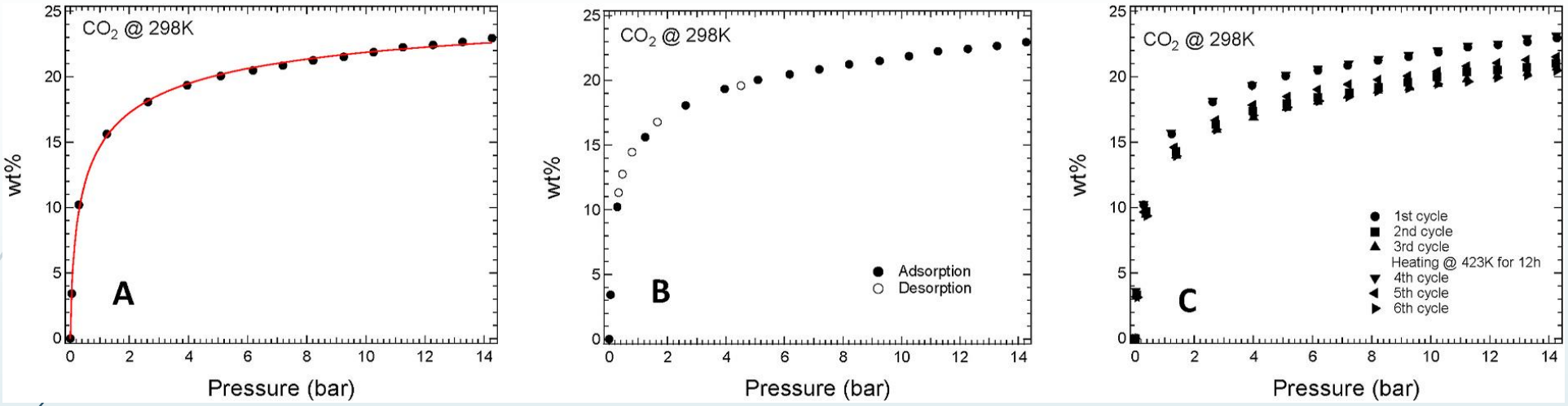
CO_2 adsorption isotherms on G-NaX sample at 298 K up to 15 bar.

A) Single adsorption isotherms (the red line between points is obtained by using the fit of Toth.

B) Adsorption (solid markers) and desorption (empty markers) isotherms.

C) Multiple adsorption isotherms. For all the above isotherms, the magnitude of the error is the symbol itself.

CO_2 adsorption



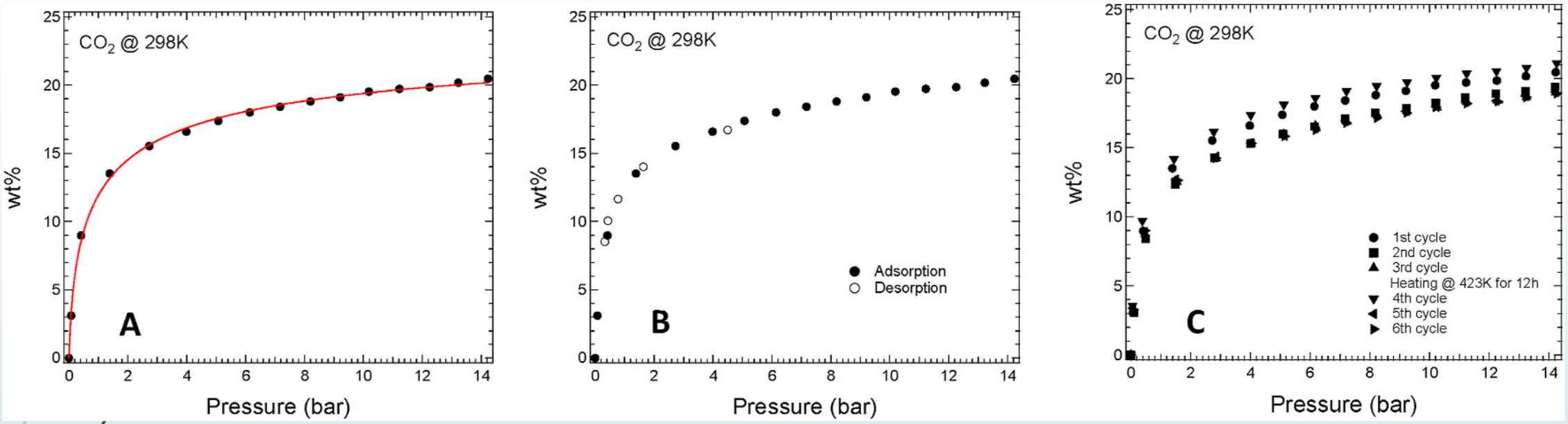
CO_2 adsorption isotherms on G-NaX-f sample at 298 K up to 15 bar.

A) Single adsorption isotherms (the red line between points is obtained by using the fit of Toth.

B) Adsorption (solid markers) and desorption (empty markers) isotherms.

C) Multiple adsorption isotherms. For all the above isotherms, the magnitude of the error is the symbol itself.

CO_2 adsorption



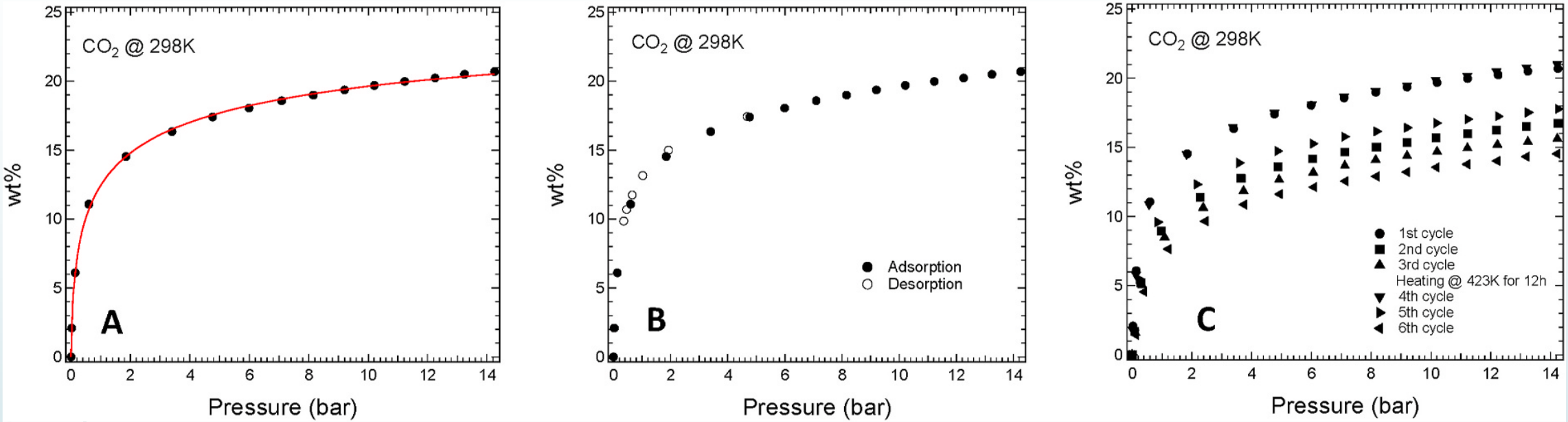
CO_2 adsorption isotherms on G-NaX-AC-f sample at 298 K up to 15 bar.

A) Single adsorption isotherms (the red line between points is obtained by using the fit of Toth.

B) Adsorption (solid markers) and desorption (empty markers) isotherms.

C) Multiple adsorption isotherms. For all the above isotherms, the magnitude of the error is the symbol itself.

CO_2 adsorption



CO_2 adsorption isotherms on G-NaX-AC sample at 298 K up to 15 bar.

A) Single adsorption isotherms (the red line between points is obtained by using the fit of Toth.

B) Adsorption (solid markers) and desorption (empty markers) isotherms.

C) Multiple adsorption isotherms. For all the above isotherms, the magnitude of the error is the symbol itself

CO_2 adsorption fitting

Amount of CO_2 adsorbed at 15 bar and 298 K in each adsorption cycle.

Sample	1st cycle (wt%)	2nd cycle (wt%)	3rd cycle (wt%)	Heating @ 473 K	4th cycle (wt%)	5th cycle (wt%)	6th cycle (wt%)
G-NaX-f	22.95	21.03	20.68	12 h	23.14	21.51	20.45
G-NaX-AC-f	20.46	19.42	19.01	12 h	21.12	19.02	18.91
G-NaX-AC	20.69	16.74	15.63	12 h	21.02	17.78	14.54
G-NaX	18.81	11.02	11.58	12 h	18.70	11.75	11.12

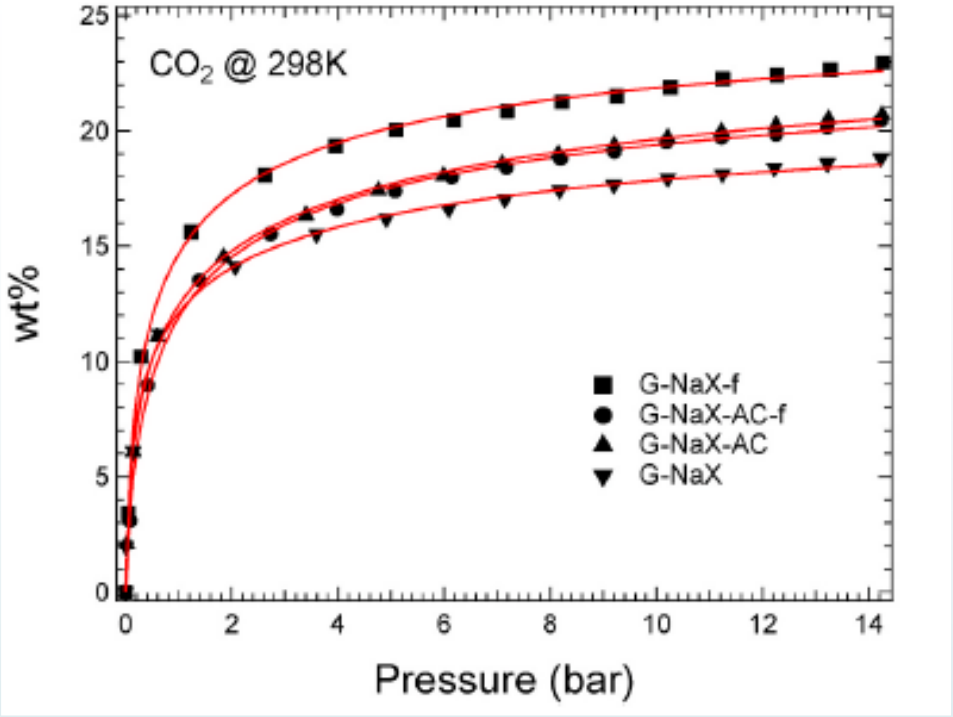


Table 7
Maximum CO_2 storage capacity, equilibrium constant and homogeneity grade for all analyzed samples obtained as Toth equation fitting parameters.

Sample	$wt\%_{max} \pm \Delta\ wt\%_{max}$ [$g_{CO2}/g_{adsorbent}$*100]	mmol/gmax ± Δ mmol/gmax [mmol/g]	$K \pm \Delta K$ [bar^{-1}]	$t \pm \Delta t$ [-]
G-NaX-f	27.04 ± 0.84	5.46 ± 0.19	7.50 ± 1.43	0.51 ± 0.04
G-NaX-AC-f	24.81 ± 0.84	5.64 ± 0.19	4.02 ± 0.67	0.53 ± 0.04
G-NaX-AC	28.12 ± 1.02	6.39 ± 0.23	11.19 ± 2.01	0.40 ± 0.02
G-NaX	23.93 ± 0.43	5.44 ± 0.10	18.60 ± 2.42	0.40 ± 0.02

Conclusion

- The proposed preparation processes allow combining and exploiting the binding properties of geopolymer, the adsorption properties of zeolite NaX, the tailored pore structure and high stability of activated biochar and the macroporosity introduced by the foaming agent to appropriately tune the final properties of the resulting adsorbent for the desired CO_2 capture.

- The possibility of producing macroporosity without inhibiting the polymerization and crystallization reactions or affecting the topology of the produced zeolite pave the way to further optimization of pore structure

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