

# IN SILICO EXPERIMENTS ON VERTICALLY ALIGNED CARBON NANOTUBES FOR MONOVALENT CATION SELECTIVE MEMBRANES

G. De Luca<sup>1,4</sup>, J. Luque Di Salvo<sup>2</sup>, A. Cipollina<sup>3,4</sup>, G.L. Luque<sup>2</sup>, E.P.M. Leiva<sup>2</sup>, G. Micale<sup>3,4</sup>

<sup>1</sup>ITM-CNR, Rende (CS)

<sup>2</sup>INFIQC, Córdoba, Argentina

<sup>3</sup>Università di Palermo

<sup>4</sup>Consorzio INSTM



**Sostenibilità in Lombardia**

**VERSO IL 3° FORUM 19-22 OTTOBRE 2022**

**Objective:** Define diameters and symmetry of Carbon NanoTubes (CNTs) to be used in vertically aligned CNTs membranes for the separation of mono-valent ions from divalent ones

**Why** Monovalent ion selectivity is critical for many (electro)membrane-based technologies, like:

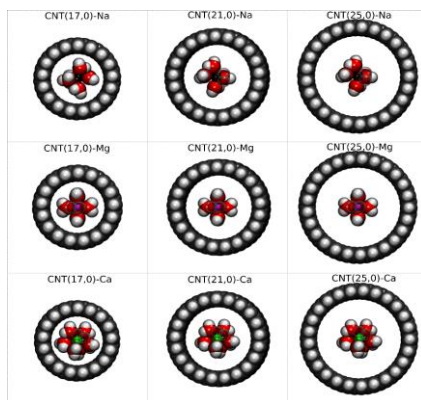
- **Electrodialysis** (Desalination and wastewater management, including metal recovery);
- **Reverse Electrodialysis** (CO<sub>2</sub>-free energy production from salinity gradients, e.g. river/seawater mixing);
- **Agricultural irrigation from (waste)water** requiring divalent cations to avoid addition of extra fertilizers.

**Results**

water-CNT-water  
All-atom 3D-pbc MD model

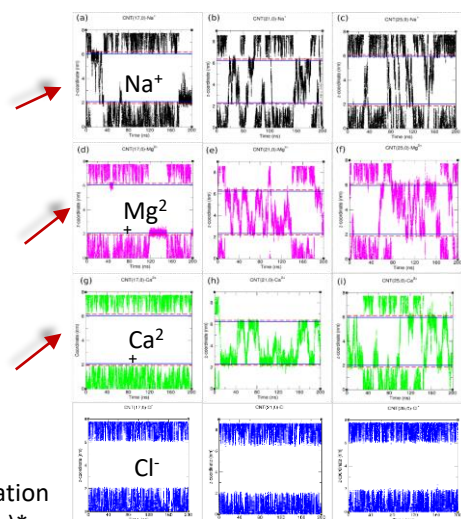


Top view of hydrated cations on the CNT inlet with calibrated diameters

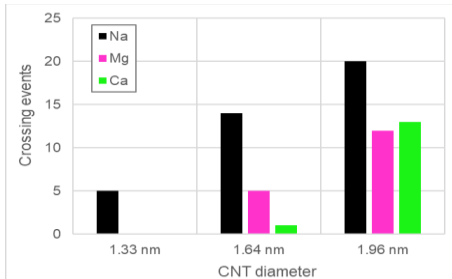


d=1.33nm d=1.64nm d=1.96nm

Cation coordinates over simulation time (200 ns), inside the CNT

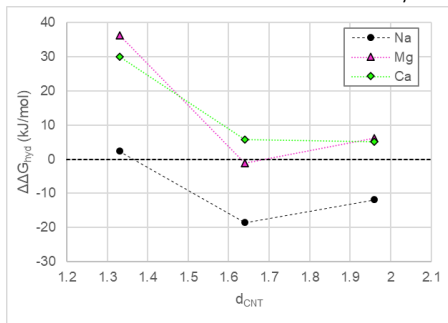


Number of crossing events from the 200ns trajectories\*



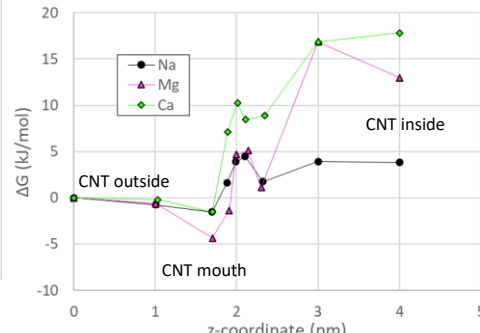
\*Extending the simulation time for the smallest CNT(17,0) was to 1µs yielded the same results

Solvation energy difference of the cation inside and outside the CNT ( $\Delta\Delta G_{hyd}$ )\*



\*cation in water bulk and inside an infinite periodic water-filled CNT,

Free energy change for cation insertion along the CNT axis ( $\Delta G$ )\*



\*Performed on the smallest CNT (17,0),

G. De Luca et al., *Desalination* 544 (2022) 116123

[g.deluca@itm.cnr.it](mailto:g.deluca@itm.cnr.it)

## Highlights

1- Na<sup>+</sup> 36 kJ/mol affinity vs. Mg<sup>2+</sup> and Ca<sup>2+</sup> total rejection with CNT 1.33 nm diameter, **opposite to polymer-based cation exchange membranes.**

2- Total rejection of Cl<sup>-</sup> anions through zig-zag CNTs 1.33 – 1.96 nm diameter.