JCAT 53 **53èmes Journées de Calorimétrie et d'Analyse Thermique**,
22-24 Mai 2023

B. PRELOT, Manel ARAISSI, Ganna DARMOGRAI, J. ZAJAC

THE USEFULNESS OF CALORIMETRY IN ENVIRONMENTAL REMEDIATION STUDIES: *EXAMPLES OF MECHANISMS OF IONIC POLLUTANT ADSORPTION FROM MULTICOMPONENT AQUEOUS SOLUTIONS*

Institut Charles Gerhardt (ICGM), CNRS, ENSCM, Univ Montpellier,
1919, route de Mende, Pôle de recherche Balard, 34095 Montpellier cedex 5 - France

Outline:

❶ **Water pollution and Solid-Liquid adsorption:**
ionic pollutants

❷ **Contribution of calorimetry to mechanistic studies**
under competitive conditions

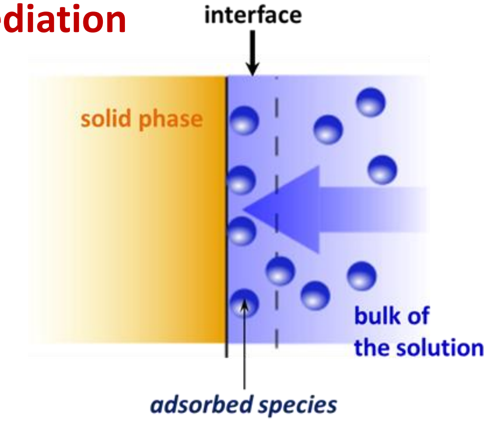
❸ **Two ways of applying Isothermal Titration Calorimetry**
- ❑ *Adsorption of anionic dyes onto layered double hydroxide*
- ❑ *Adsorption of heavy metal cations onto zeolite*

❹ **Conclusions**

Water pollution and Solid-Liquid adsorption

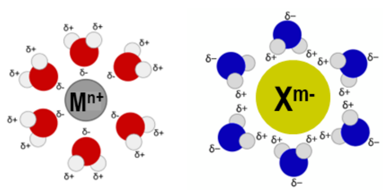
The self-purification capacity of water bodies has been exceeded !!!

Sorption at the Solid-Liquid interface for water remediation

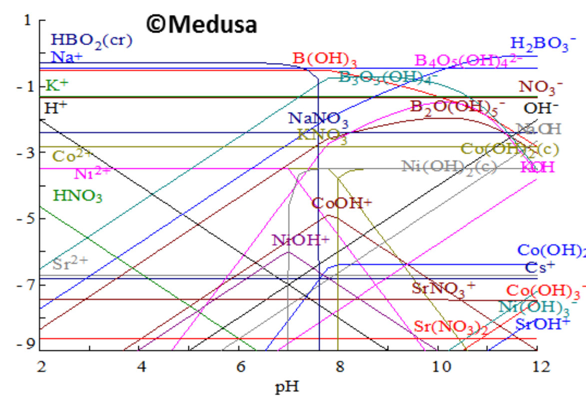


Competition

Decreased performance



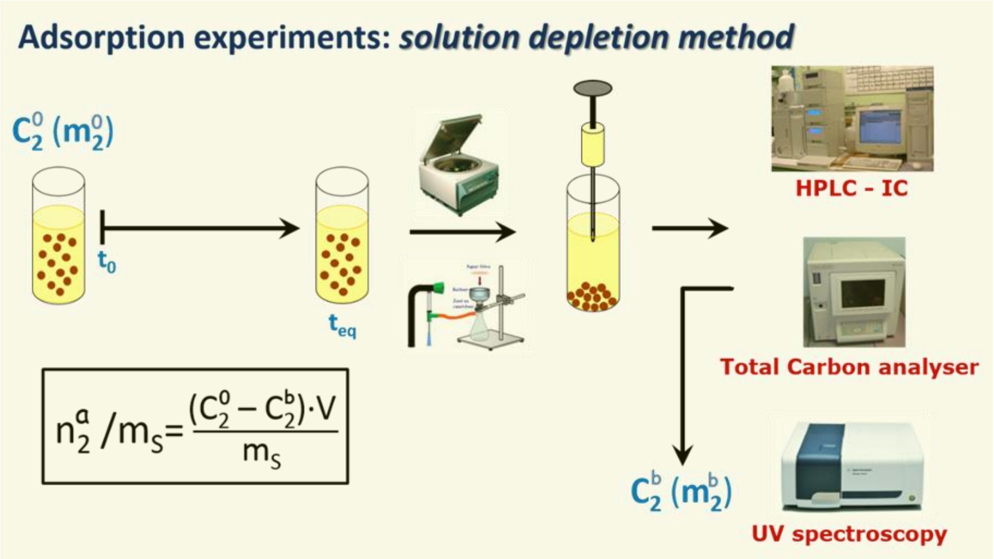
Formation of hydrated cations or anions in bulk water (pH, ionic strength)

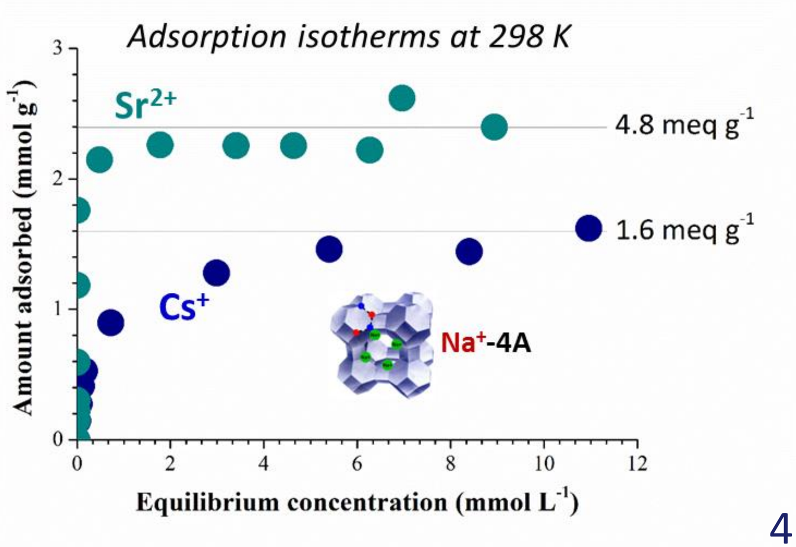


Retention of main pollutant from multicomponent solutions

Contribution of calorimetry to mechanistic studies

Quantity of adsorption



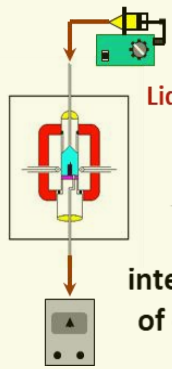


Contribution of calorimetry to mechanistic studies

Enthalpy changes: *microcalorimetry*

Titration calorimetry: variable pH, I

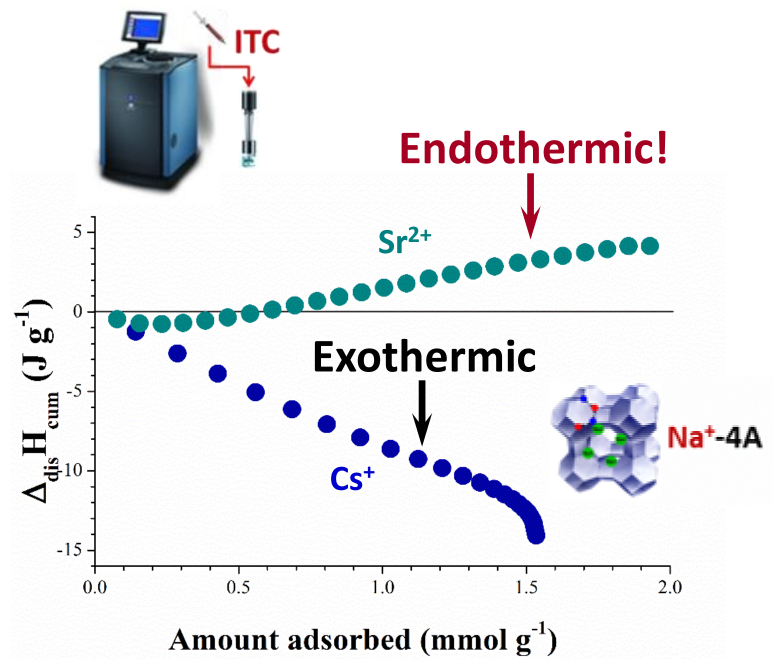
differential or cumulative enthalpy of displacement, $\Delta_{dpl}h$



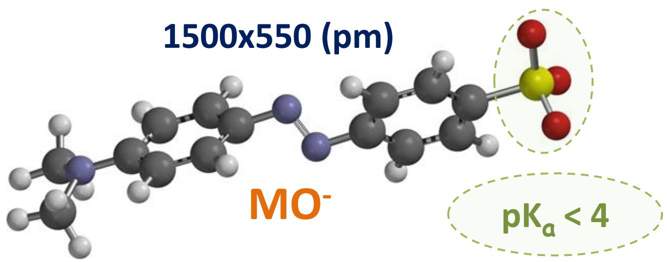
Liquid flow calorimetry: pH, I = const

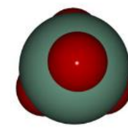
integral molar enthalpy of displacement, $\Delta_{dpl}h$

Total enthalpy balance upon adsorption

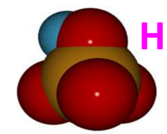


Example 1 : Adsorption of anionic dyes onto LDH

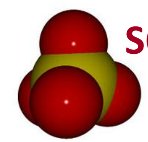




r = 255 pm + 33 pm (2.8 H_2O)
$\Delta_{hyd}G$ = -950 kJ mol^{-1}

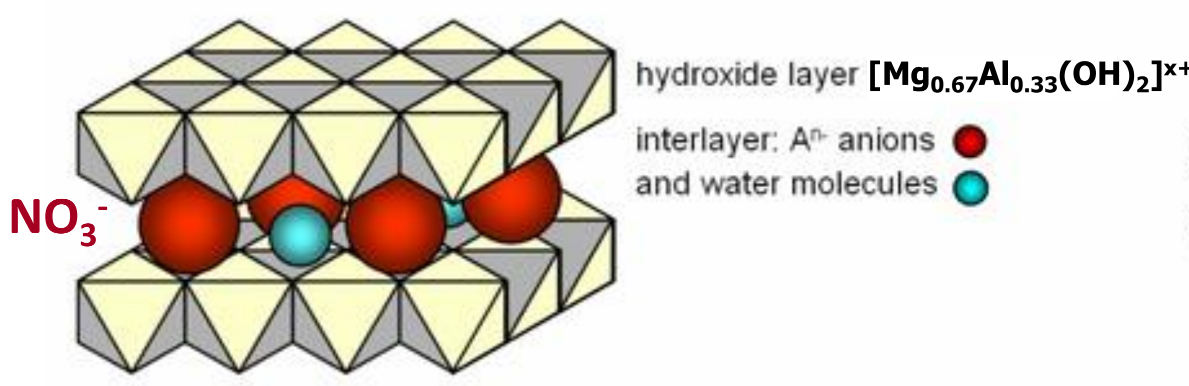


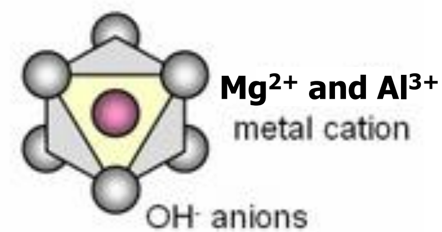
r = 238 pm + 40 pm (3.0 H_2O)



r = 240 pm + 38 pm (3.0 H_2O)
$\Delta_{hyd}G$ = -1080 kJ mol^{-1}

Layered Double Hydroxide (LDH)





J. Phys. Chem. C 119 (2015) 23388−23397 *J. Phys. Chem. C* 120 (2016) 10410−10418

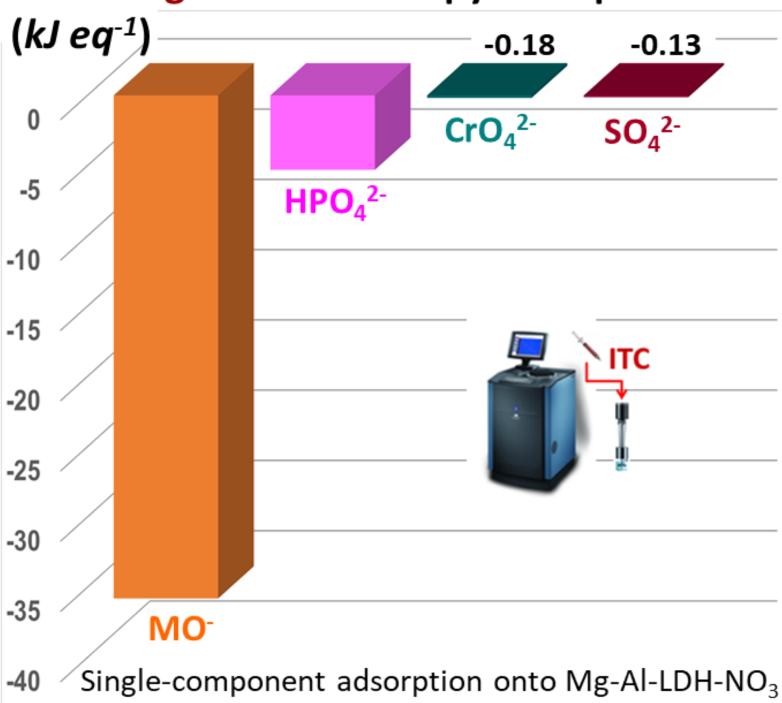
Example 1 : Adsorption of anionic dyes onto LDH

as measured from single solute solutions

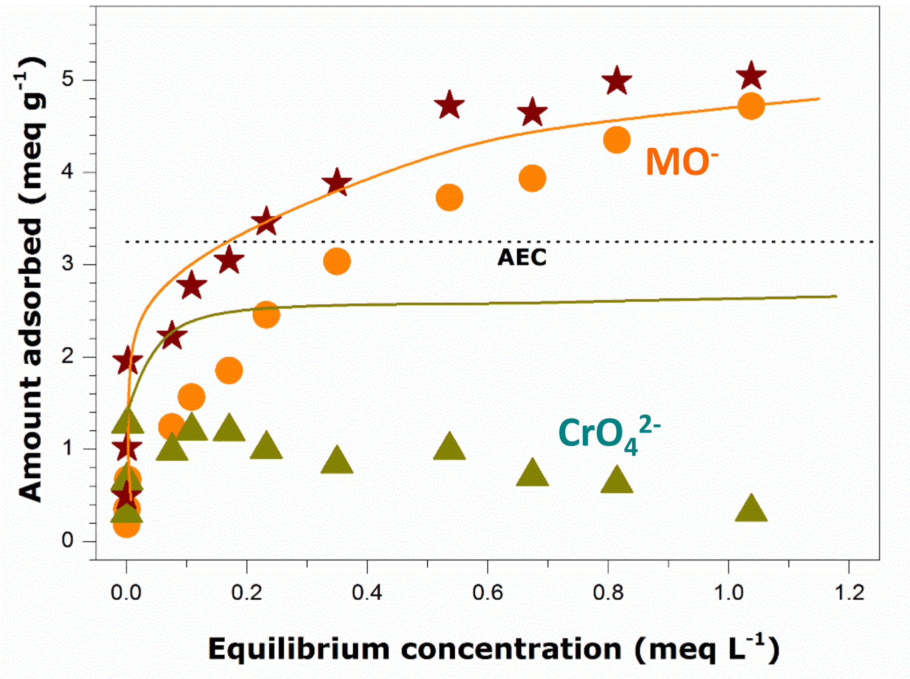
1 → **2**

Competitive adsorption of MO^- and inorganic anions onto Mg-Al-LDH-NO_3 from bi-solute solutions

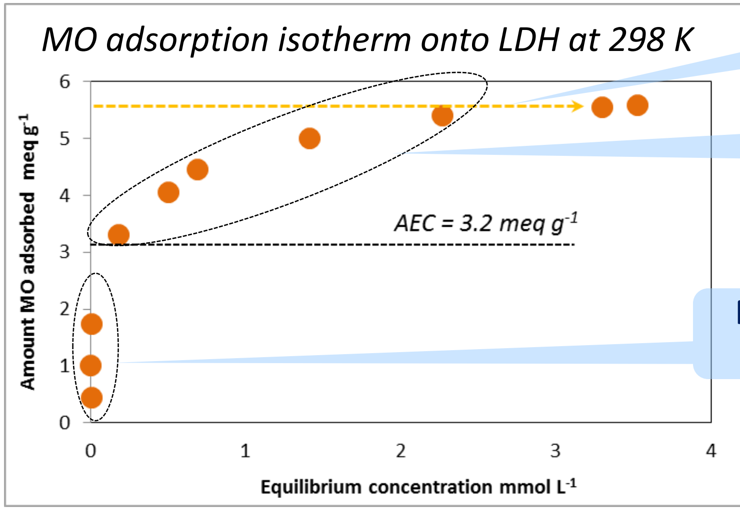
Average molar enthalpy of displacement



Individual adsorption isotherms at 298 K



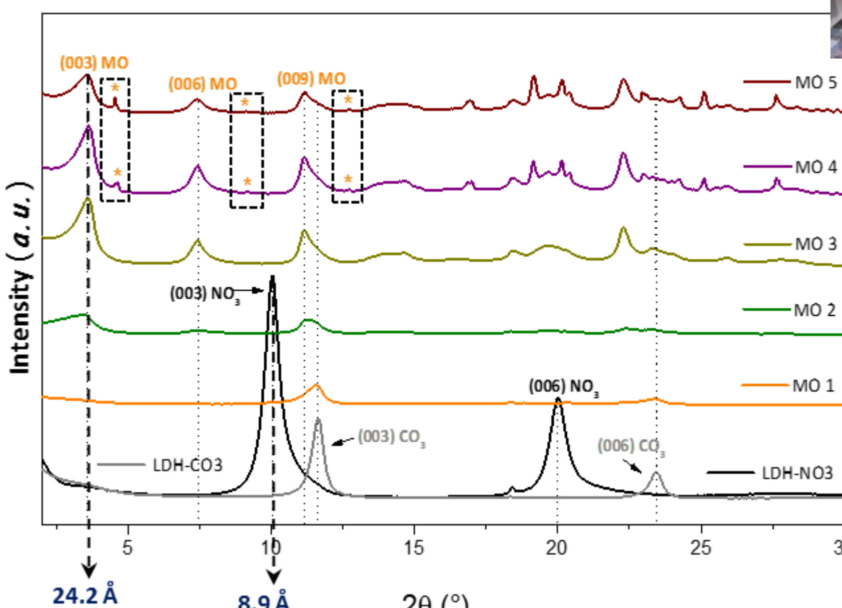
Example 1 : Adsorption of anionic dyes onto LDH



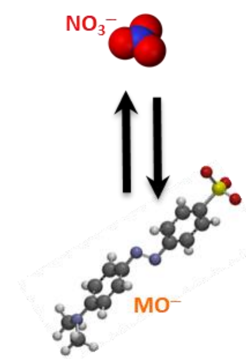
$\Delta_a n_{max}$ > AEC

MO$^-$ retention on the external surface (*co-adsorption of Na$^+$*) **weak binding affinity**

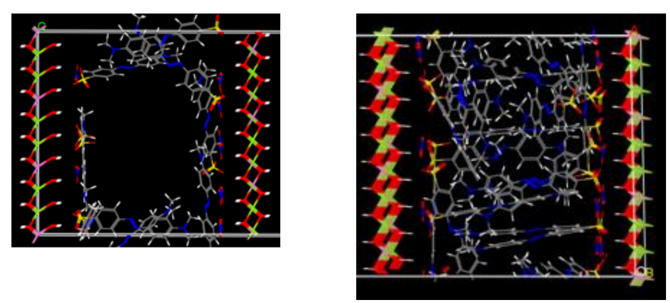
MO$^-$ intercalation within the interlayer space (*expansion of the interlayer space*) **strong binding affinity**



PHILIPS X'Pert MPD

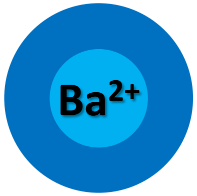


Monte Carlo simulations:

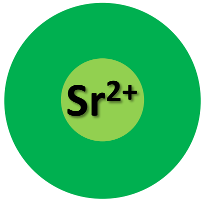


$\Delta_a n_{MO}$ →

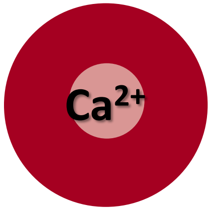
Example 2 : Adsorption of heavy metal cations onto zeolite



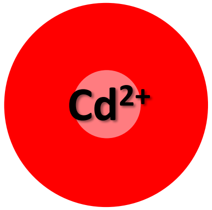
r = 136 pm + 118 pm (5.3 H_2O)
$\Delta_{hyd}G$ = -1250 kJ mol^{-1}



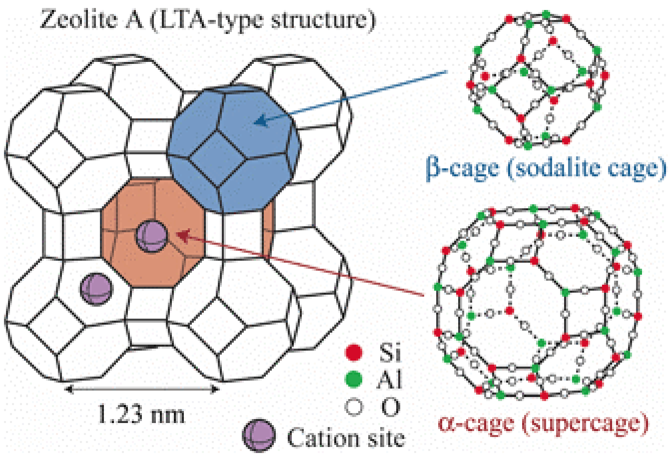
r = 113 pm + 150 pm (6.4 H_2O)
$\Delta_{hyd}G$ = -1380 kJ mol^{-1}



r = 100 pm + 171 pm (7.2 H_2O)
$\Delta_{hyd}G$ = -1505 kJ mol^{-1}



r = 95 pm + 178 pm (7.6 H_2O)
$\Delta_{hyd}G$ = -1755 kJ mol^{-1}



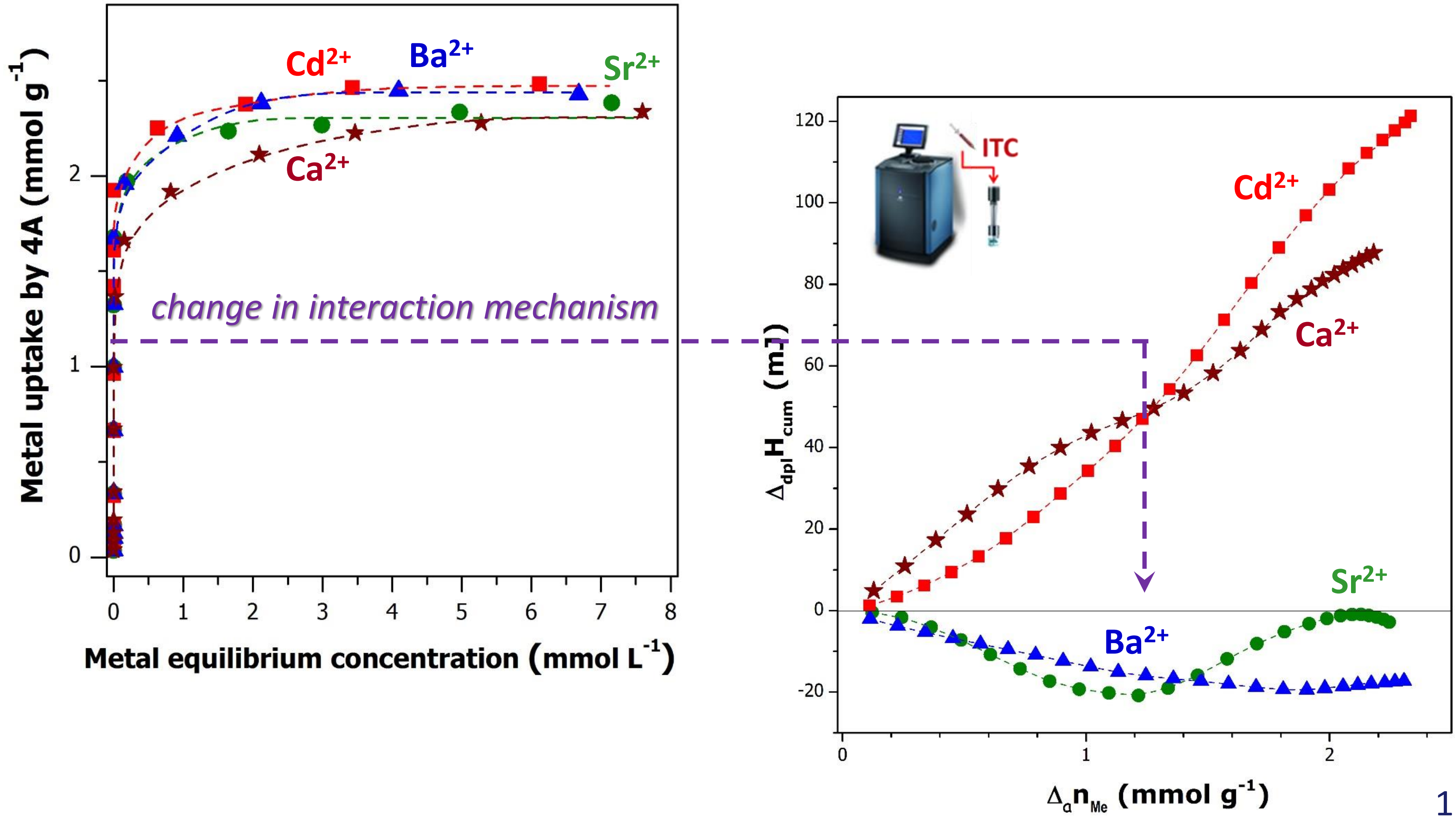
Na-4A

r = 102 pm + 116 pm (3.5 H_2O)
$\Delta_{hyd}G$ = -365 kJ mol^{-1}

Thermochimica Acta, 2018, 664, 39-47

Example 2 : Adsorption of heavy metal cations onto zeolite

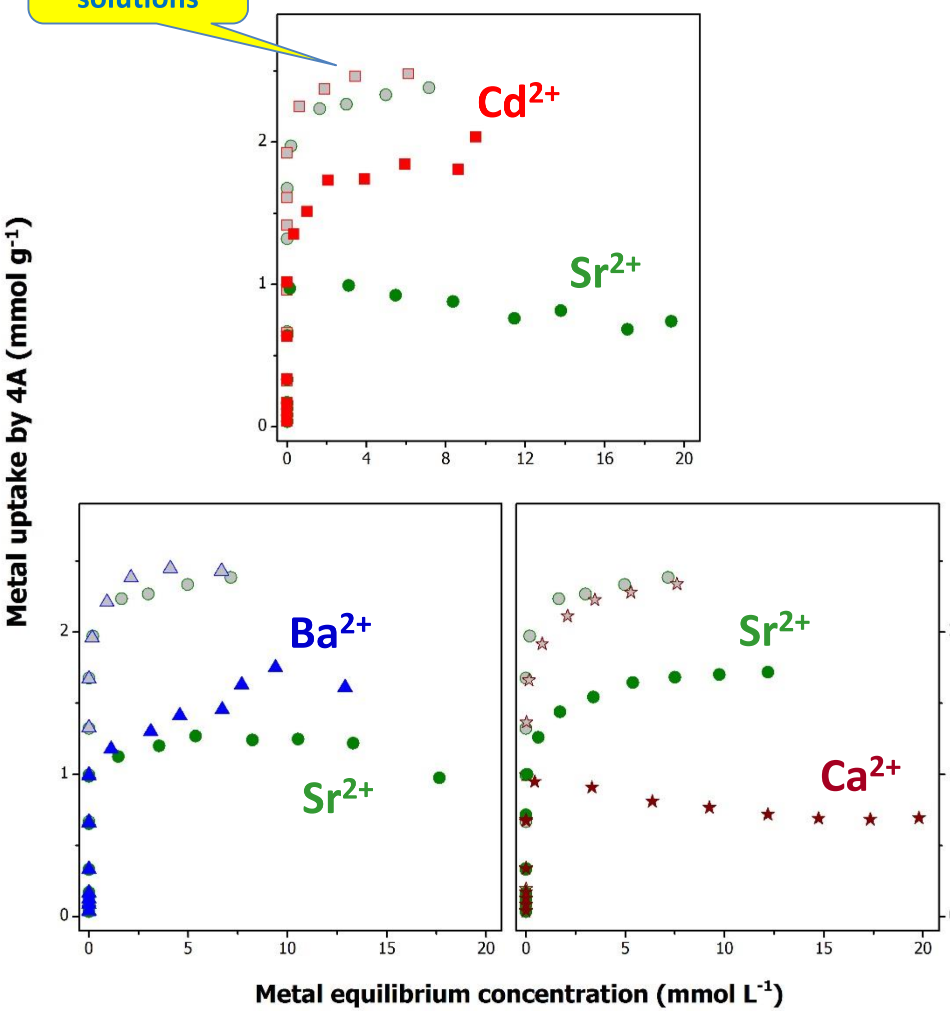
Individual adsorption from ***single-metal*** *solutions at 298 K*

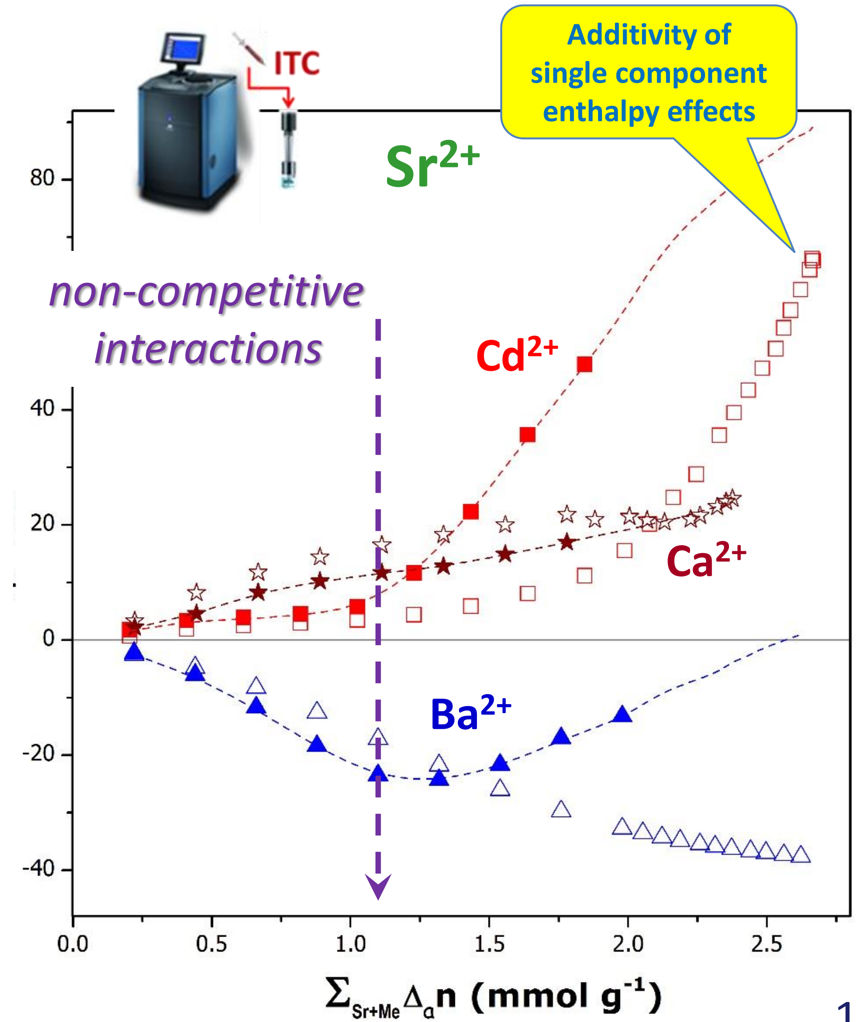


Example 3 : Adsorption of heavy metal cations onto zeolite

single solute solutions

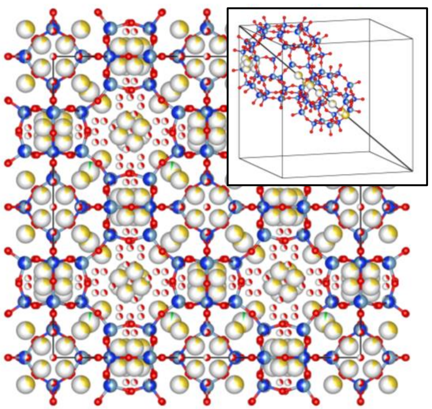
Competitive adsorption from ***two-metal*** *solutions at 298 K*





Example 2 : Adsorption of heavy metal cations onto zeolite

Rietveld refinement of X-ray diffraction patterns recorded on Na^{+}-4A containing Sr^{2+} or Cs^{+}

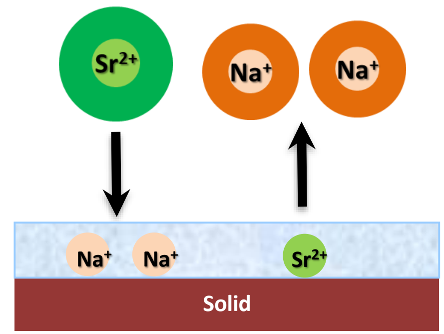


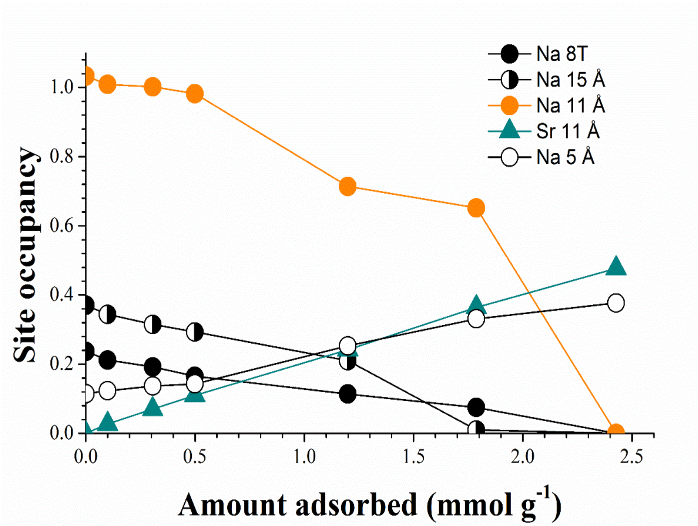
Positions of extra-framework ions and molecules

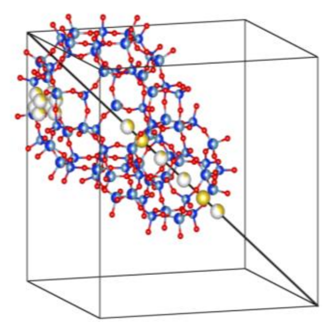
PHILIPS X'Pert MPD

Total displacement effect:

- ion exchange $M^{n+} \rightarrow Na^{+}$
- cation dehydration-rehydration







Ion exchange mechanism between ionic double layer and bulk solution:
replacement of Na^{+} by Sr^{2+} occurs only on one type of primary Na-sites

Conclusions

- Efficient adsorbents should be tested under conditions of competition amongst various solution components
- Calorimetry is a useful tool for continuous monitoring and assessment of the main interactions and competition effects involved in adsorption phenomena
- Calorimetry measurements are to be supplemented by other experimental and modelling studies

Institut Charles Gerhardt Montpellier

Thank you very much for your kind attention

CHEMISTRY: MOLECULES TO MATERIALS

POLE chimie Balard · cnrs · Université de Montpellier · enscm CHIMIE Montpellier · INSTITUT CARNOT CHIMIE BALARD