Bio-Nanohybrid Materials

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AIM OF THIS COMMUNICATION

-Overview of procedures to obtain biopolymer nanocomposites provided with specific functionality

-Applications of such materials towards advanced devices

-Research results from our own laboratory

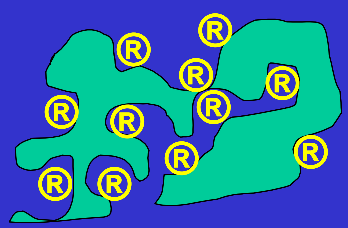
ORGANIC-INORGANIC HYBRID MATERIALS

- **Grafting of organic groups**

EXAMPLES

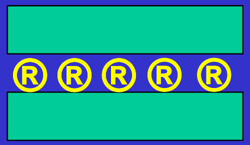
grafting of organosilanes on silicic surfaces

- **Sol-gel methods**



self-templating synthesis of organosilicic compounds

- **Intercalation of organic compounds**

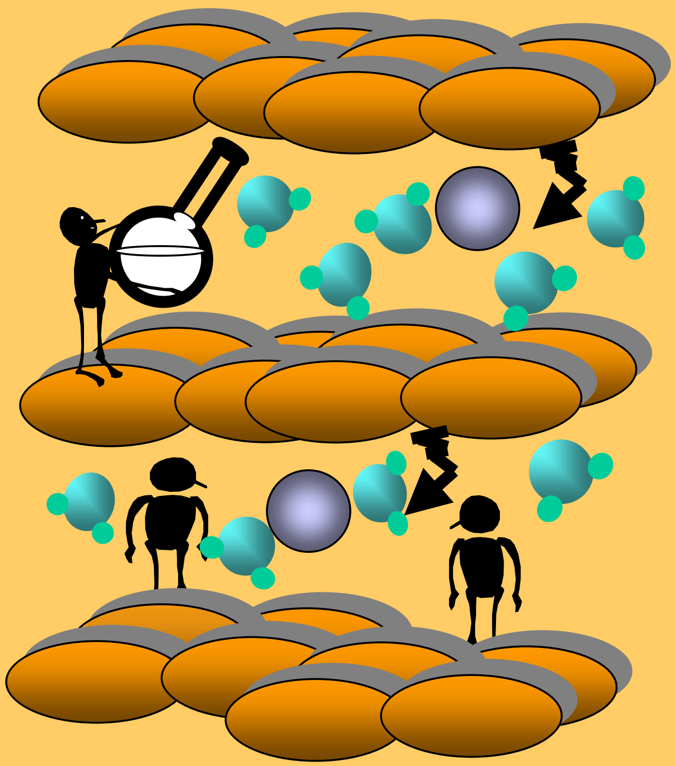


polymer & biopolymer

nanocomposites

Nanostructured Organic-Inorganic Functional materials have to be prepared by a combination of physical and chemical methods following the modus operandi characteristic of the procedures of molecular engineering.

Idealized representation of a "nanochemist" applying methods for deliberate modifications of the functional properties of a 2D solid material. The picture includes some laborers of theoretical formation studying physical processes into the solid.



E. RUIZ-HITZKY "*Organic-Inorganic Materials: From Intercalations to Devices*". Chapter 2. In: P. Gómez-Romero, C. Sánchez, eds. Functional Hybrid Materials; Wiley-VCH Verlag GmbH, 2004.

STRUCTURAL & FUNCTIONAL NANOCOMPOSITES

COMPOSITE MATERIALS

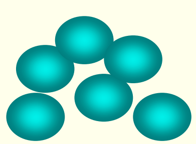
Are solids resulting from the combination of two or more simple materials that develop a ***continuous phase*** *and a* ***dispersed phase*** *which together have a set of properties that is essentially different from the components taken separately.*

polymer
metal
ceramic...

glass fiber
silica...

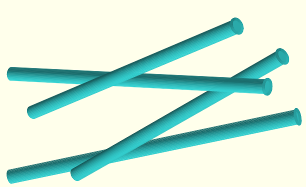
NANOCOMPOSITE MATERIALS

Are composites in which the dispersed phase presents ***at least one dimension at the nanometric scale.***



3-nano-D

Silica, C…



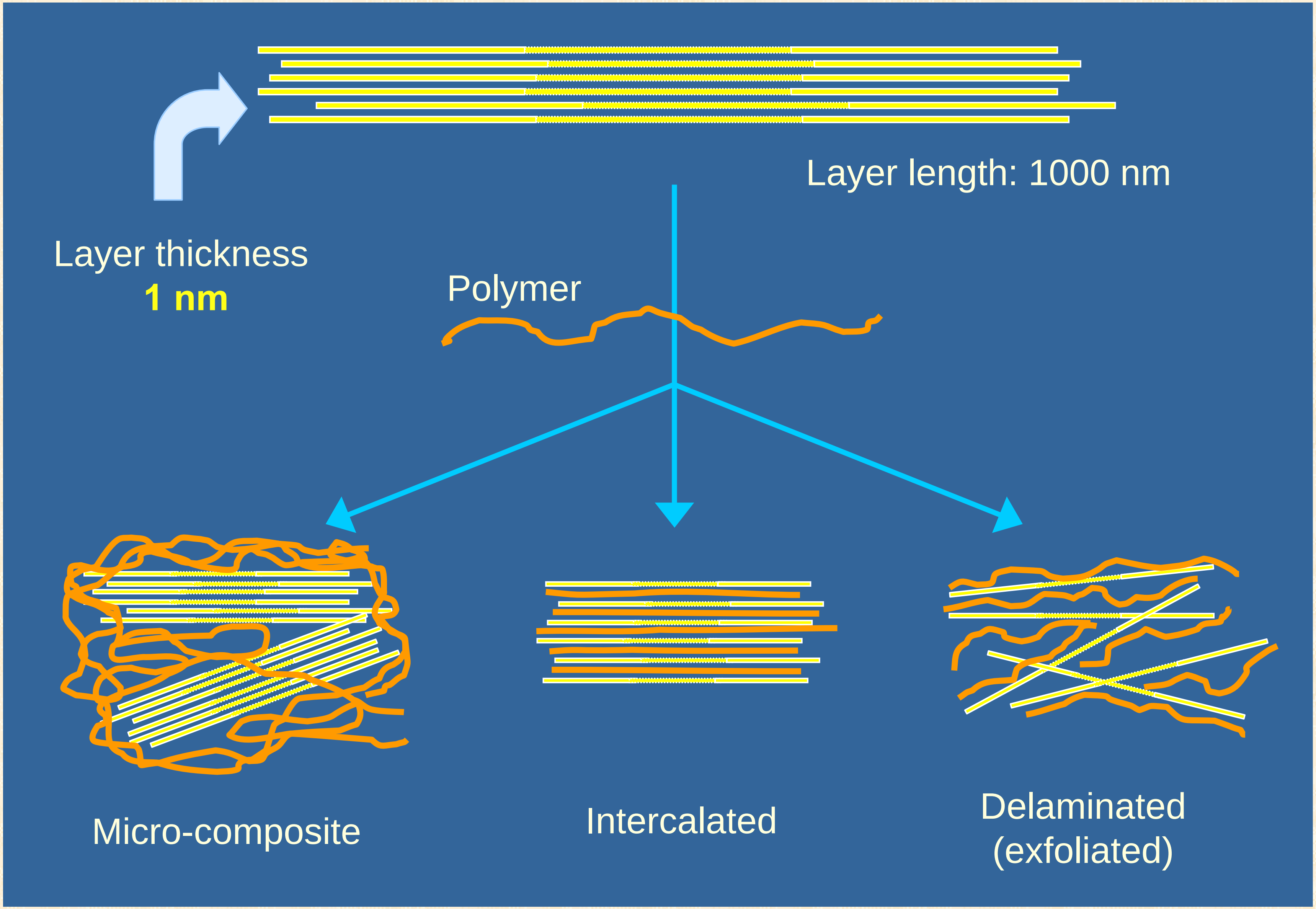
2-nano-D

Fibres, tubes…

1-nano-D

Layered solids

HYBRID NANOCOMPOSITES BASED ON ORGANIC POLYMERS AND LAYERED SOLIDS



EXAMPLES OF POLYMER-LAYERED SOLID NANOCOMPOSITES

Possibilities:

- **inorganic host**: non-charged, positively or negatively charged layers, insulator, semiconductor, redox-sites, …
- **polymers**: insulators, conducting, ionomers, polyelectrolytes…

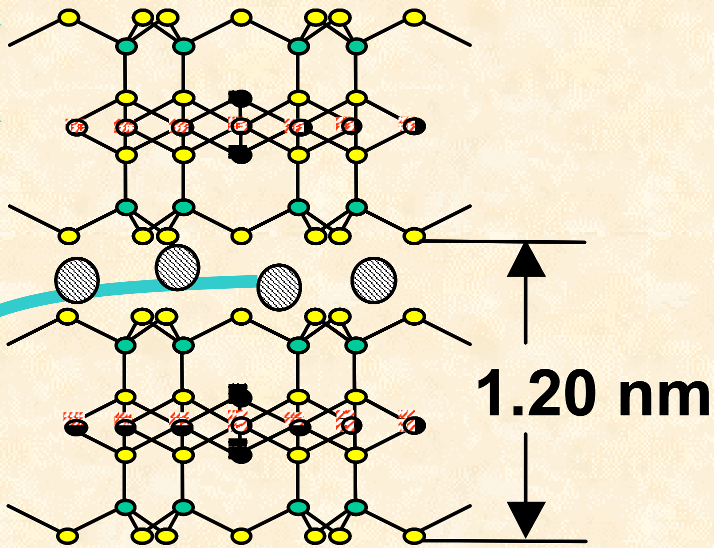
Examples:

Host	polymer
layered silicates (clays) (montmorillonite,. ..)	PVA, PS, PSS, PMMA, PAN, PEG, PEO, PANi, PPy
layered double hydroxides (MgAl, ZnAl, ZnCr,…)	PSS, PVS, PAA, PANi
phosphates & phosphonates (α-ZrP,…)	PPy, PANi,…
metal oxides ($V_2O_5 \cdot nH_2O$, CoO_2, MoO_3,..)	PVP, PPV, PANi, PPy, PTh, PEG, PEO
metal chlorides & oxychlorides (FeOCl, α-$RuCl_3$,…)	PVP, PPy, PANi, PTh, PEO
metal chalcogenides (MoS_2, $NbSe_2$,…)	PEO, PANi
metal phosphochalcogenides ($MnPS_3$, $CdPS_3$,…)	PEO, PANi,
graphite oxide	PEO, PANi

LAYERED SILICATES (CLAYS)

***Natural** or synthetic phyllosilicates. Type 2:1 charged silicates (montmorillonite, hectorite,..)*

TWO tetrahedral layers of M^{IV} (eg. Si) which are co-ordinated by oxygen anions to M^{III} (eg. Al) in ONE octahedral layer



substitution of M^{III} cations by M^{II} cations in the octahedral layer and/or substitution of M^{IV} cations by M^{III} cations in the tetrahedral layer

↓

overall negative charge

electrical neutrality is kept by exchangeable interlayer cations

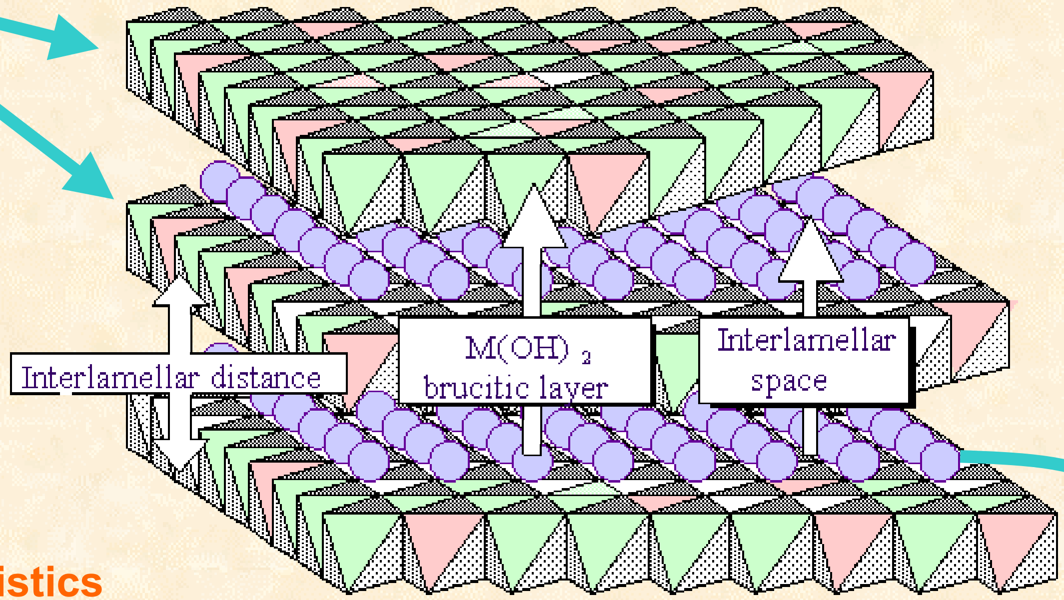
a large variety of characteristics due to:

- **nature of cations M^{II} ,M^{III} and M^{IV}**
- **nature of the interlayer cation**

LAYERED DOUBLE HYDROXIDES (LDHs)

*LDHs are **synthetic** or natural solids with a layered structure similar to that exhibited by natural $Mg(OH)_2$, brucite.*

layers of M^{II} and M^{III} cations which are octahedrally co-ordinated by six oxygen anions, as hydroxides



substitution of M^{III} cations into the brucite-like hydroxide layer

↓

overall positive charge

a large variety of characteristics due to:

- nature of cations M^{II} and M^{III}

- nature of the interlayer anion

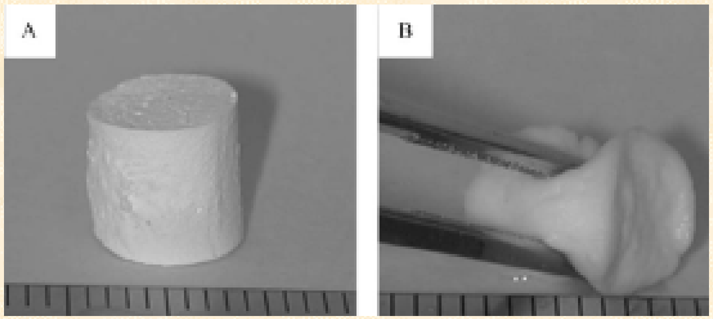
electrical neutrality is kept by exchangeable interlayer anions

Characteristics:

- **high charge density in the layers**
- **anion-exchange properties: ion-exchange capacity 2-3 times greater than clays**

Bio-nanocomposites : State of the Art & Examples

Bio-nanohybrids from collagen/alginate and hydroxyapatite: biomaterials for bone tissue engineering and drug delivery:



newly formed bone retained the original size of the bio-nanocomposite implant

(Sotome et al. *Mater. Sci. Engineering C*, 2004, *24*, 341-347)

Negatively charged DNA has been intercalated in a LDH matrix
LDH works as a nonviral vector to transfer the DNA into the cells:

(Choy, et al. *Angew. Chem. Int. Ed.*, 2000, *39*, 4042-4045)

OBJECTIVES

The development of bio-nanocomposites based on the intercalation of natural polysaccharides into layered solids (clays & LDHs)

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Reinforcement of biopolymers
Tuneable ion-exchange behaviour

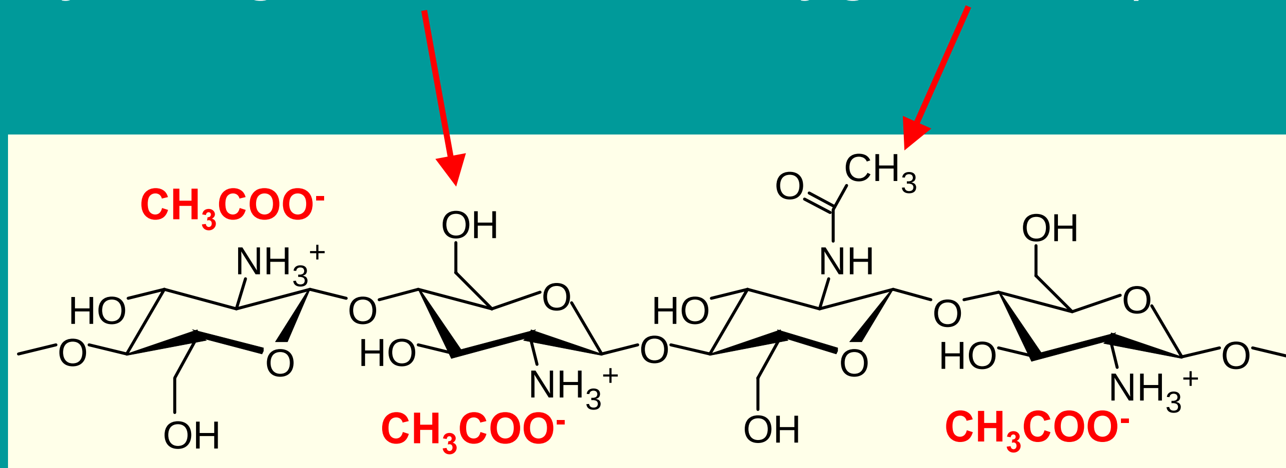
↓

•*Application of the bio-nanocomposites as active phase of potentiometric sensors*

•*Controlled release of electrically charged drugs*

CHITOSAN-CLAY BIO-NANOCOMPOSITES

Chitosan: bio-polymer constituted by saccharide units (is a copolymer of glucosamine and N-acetylglucosamine).

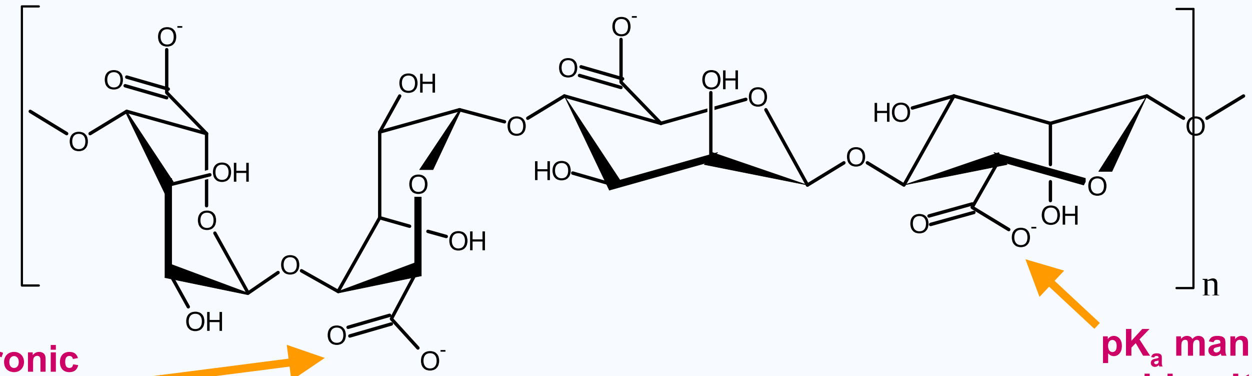


In acid solutions (acetic acid, 1%) as a positively charged polymer (**$-NH_3^+$, pK_a = 6.3**), which is adsorbed on smectite clay suspensions.

- Ion-exchange process
- Polymer-salt intercalation

M. DARDER, M. COLILLA, E. RUIZ-HITZKY ***Biopolymer-clay nanocomposites based on chitosan intercalated in montmorillonite*** **Chem. Mater. 15, 3774-3780 (2003)**

ANIONIC POLYSACCHARIDES LDH BIO-NANOCOMPOSITES



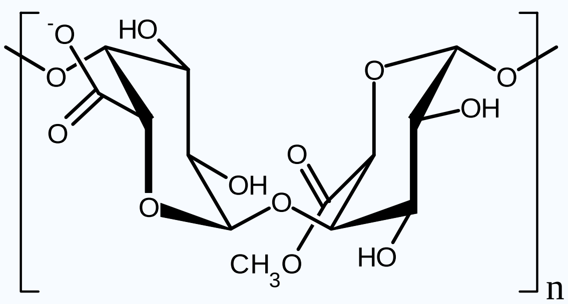
pK_a guluronic acid units = 3.65

pK_a mannuronic acid units = 3.38

Alginate

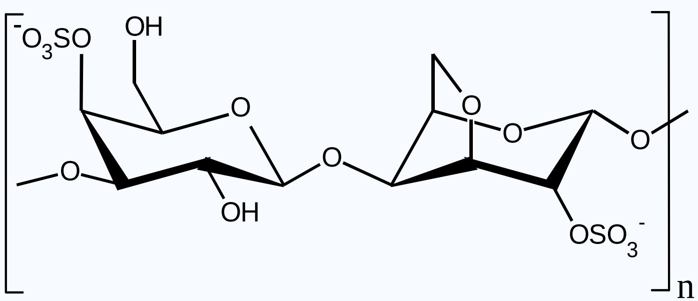
From brown algae

pK_a = 2.9



Pectin

From citrus fruits

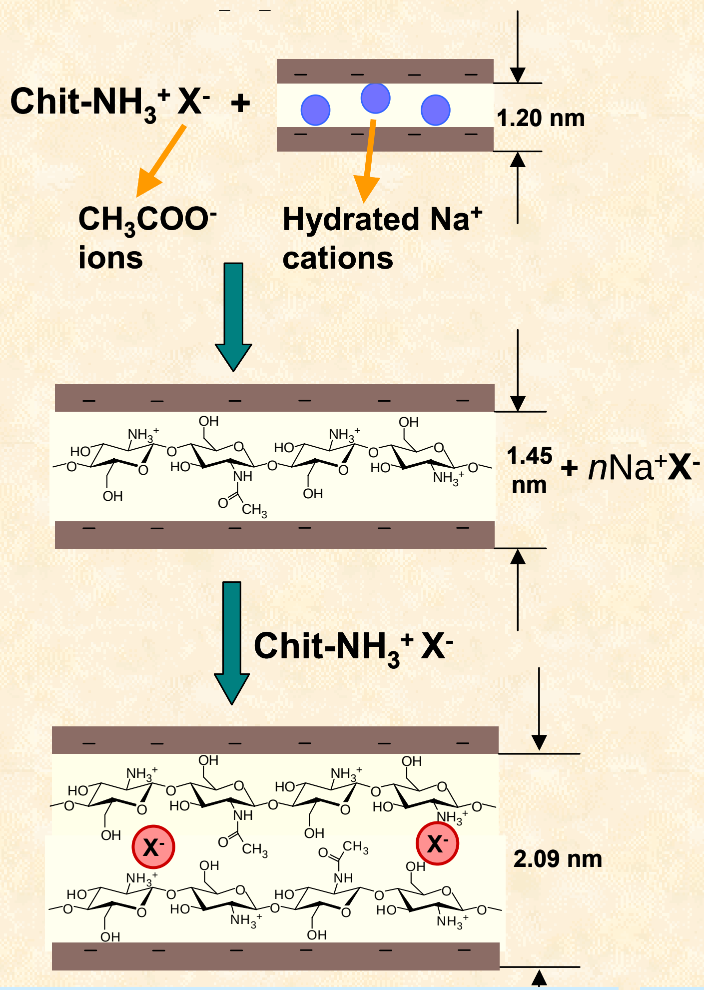


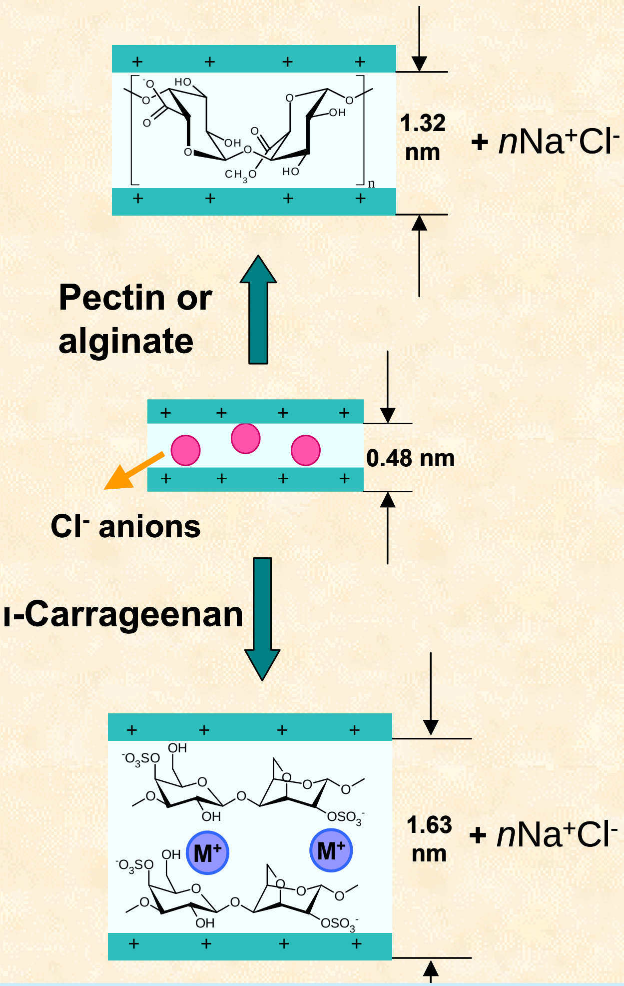
iota-Carrageenan

From red algae

chitosan-montmorillonite bio-nanocomposites

anionic polysaccharides-LDH bio-nanocomposites

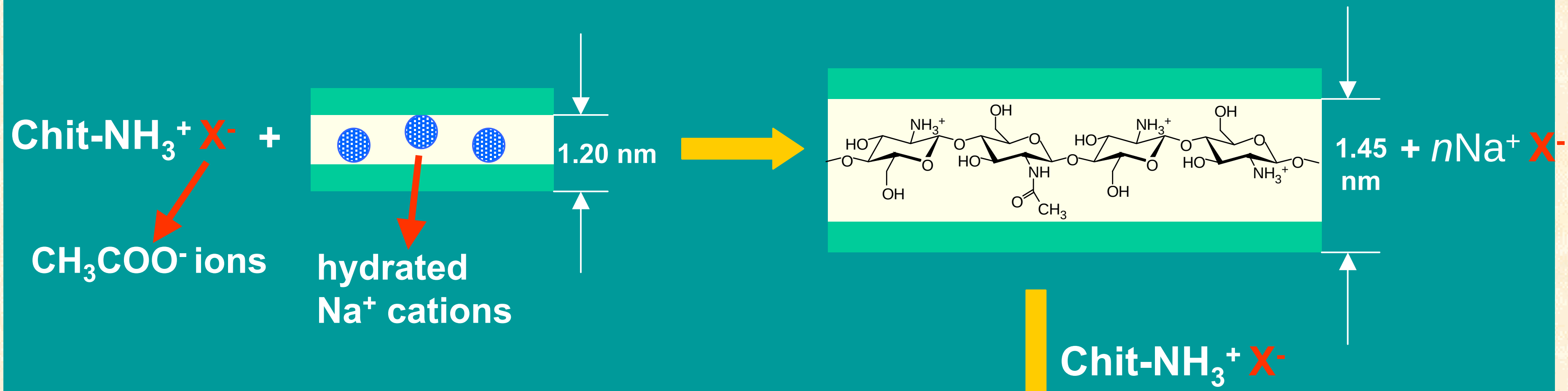


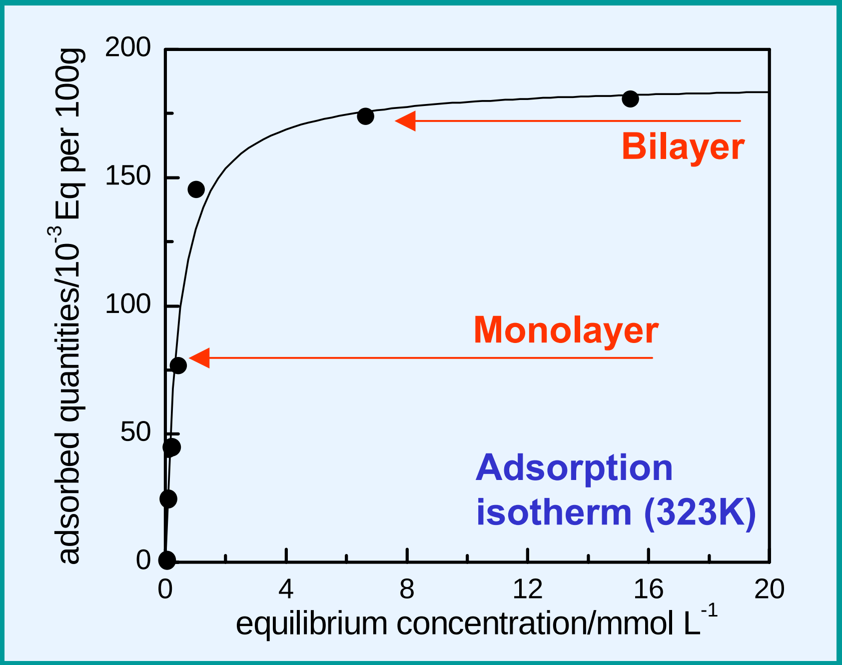


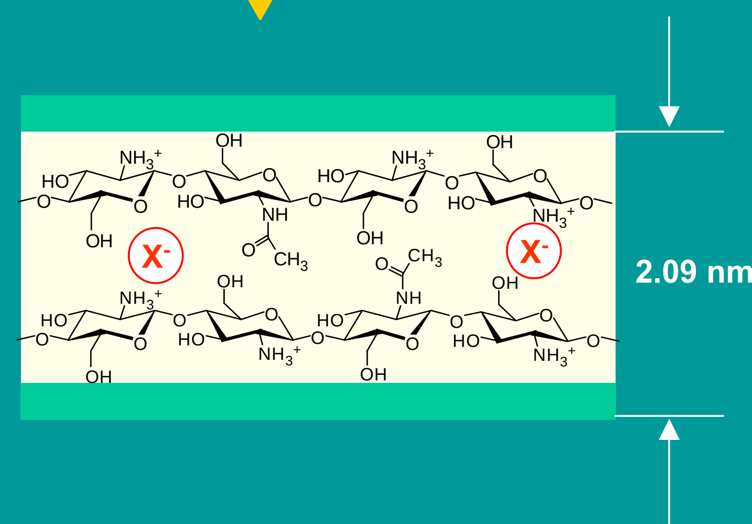
M. DARDER, M. COLILLA, E. RUIZ-HITZKY
Biopolymer-clay nanocomposites based on chitosan intercalated in montmorillonite
<u>Chem. Mater. 15</u>, 3774-3780 (2003)

M. DARDER, M. LOPEZ-BLANCO, P. ARANDA, F. LEROUX, E. RUIZ-HITZKY ***Bio-nanocomposites based on layered double hydroxides***
<u>Chem. Mater. 17,</u> 1969-1977 (2005)

Intercalation of chitosan in Na^+-montmorillonite



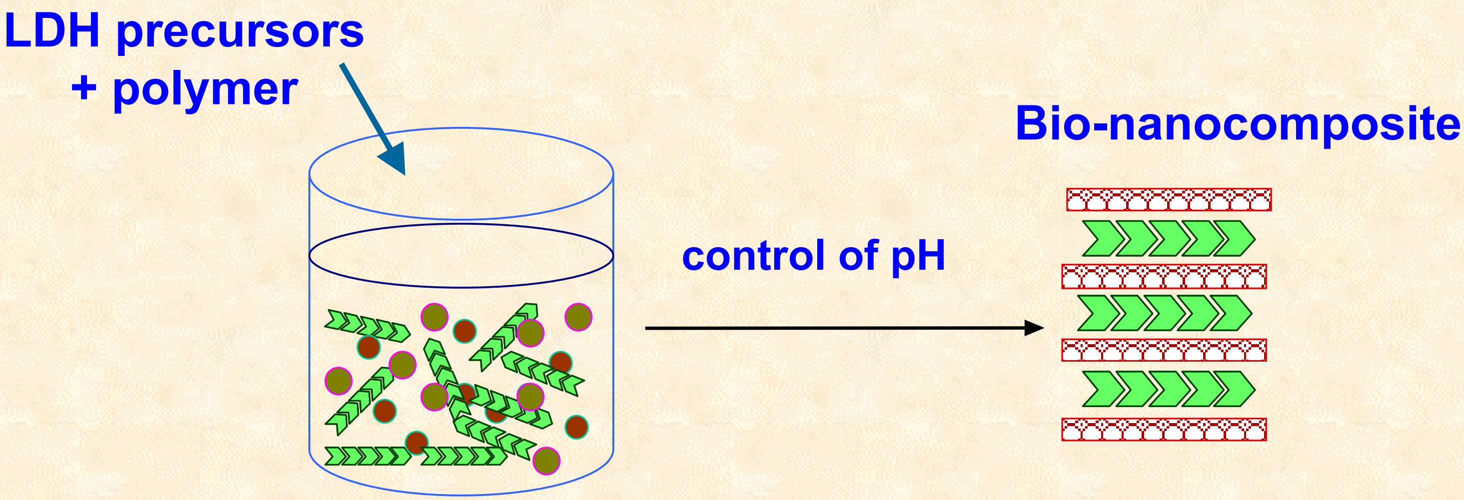




Theoretical anionic exchange capacity of 57 mEq/100g

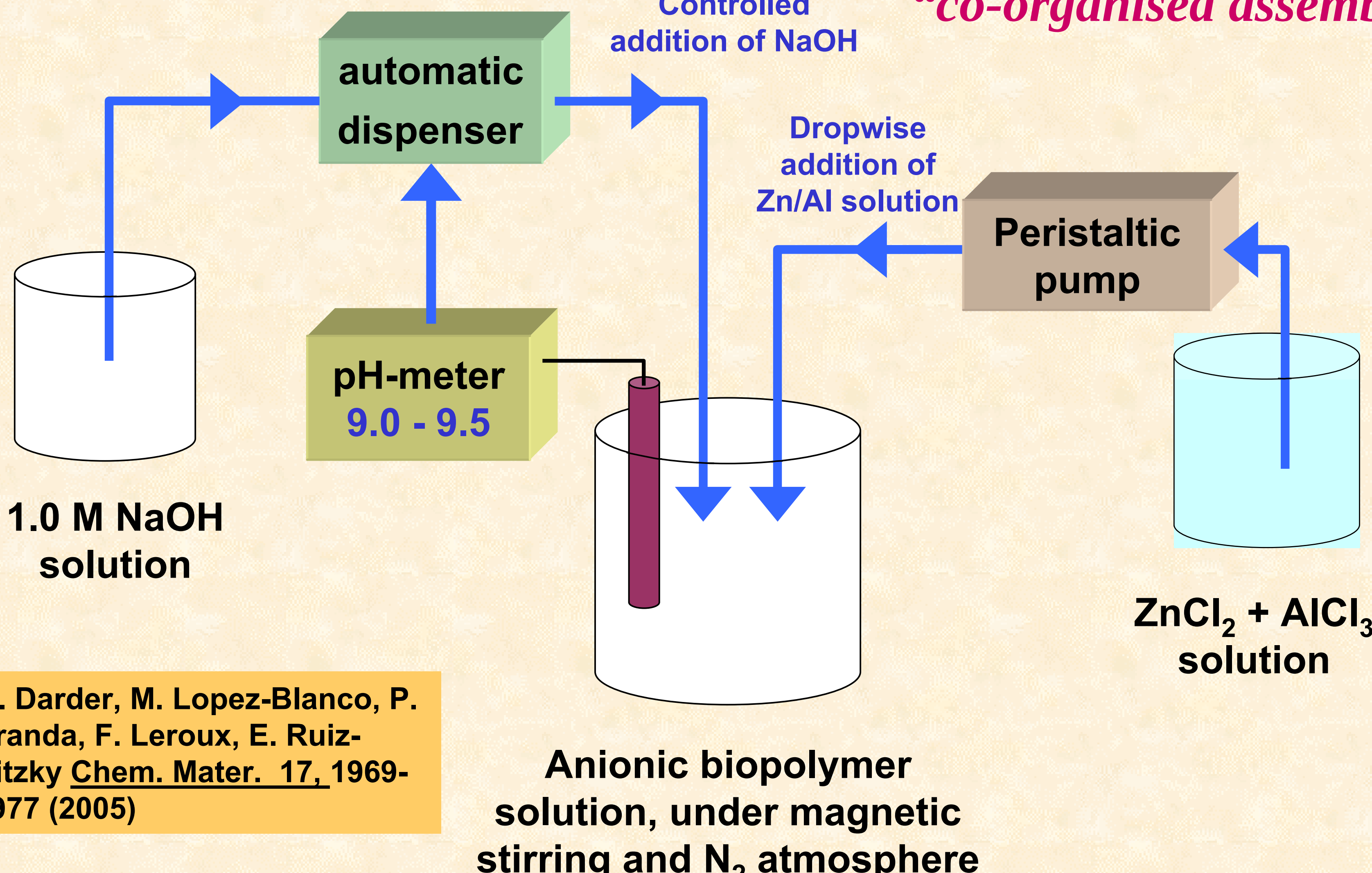
ONE-POT SYNTHESIS OF BIO-POLYMER/LDH NANOCOMPOSITES

Co-organized assembly or templating co-precipitation:



TEMPLATE SYNTHESIS OF BIOPOLYMER-LDH NANOCOMPOSITES

"coprecipitation" or "co-organised assembly"

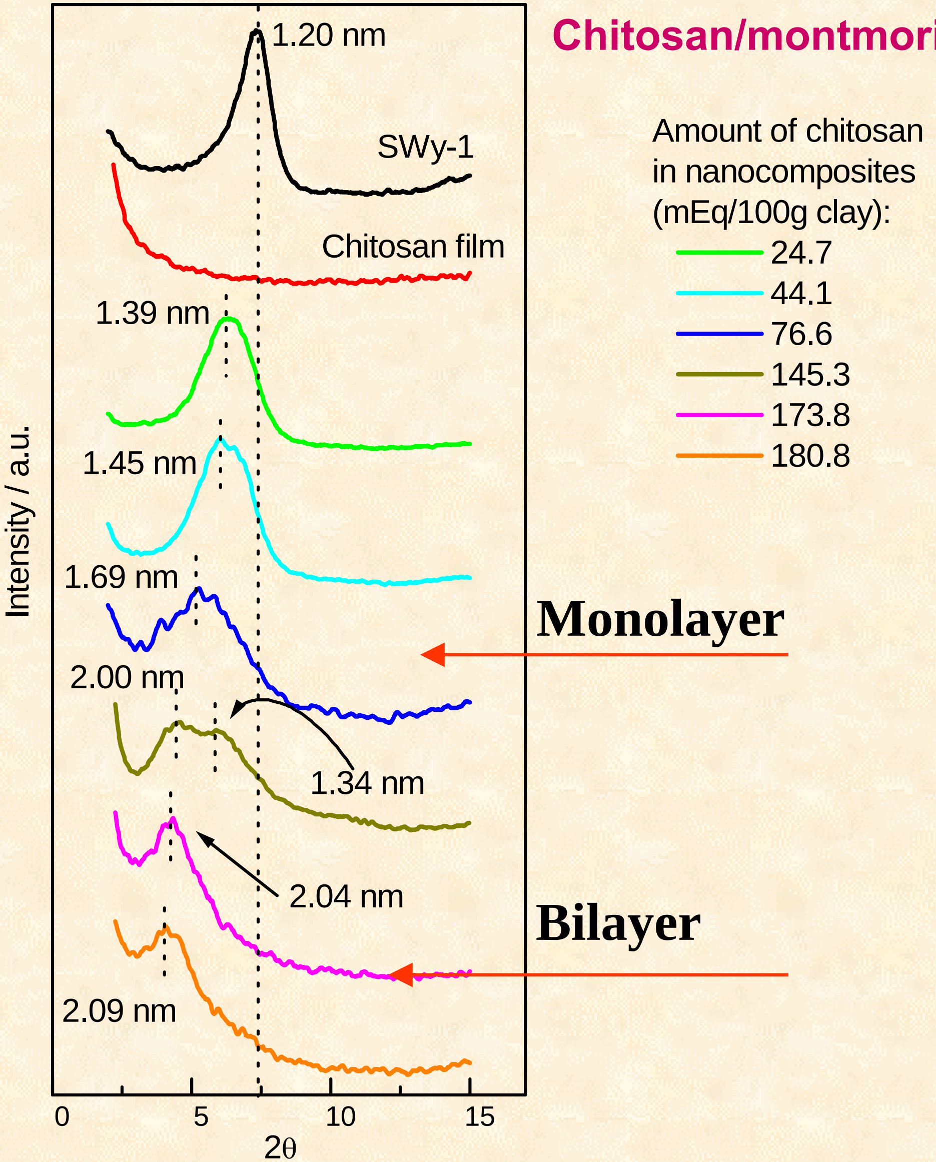


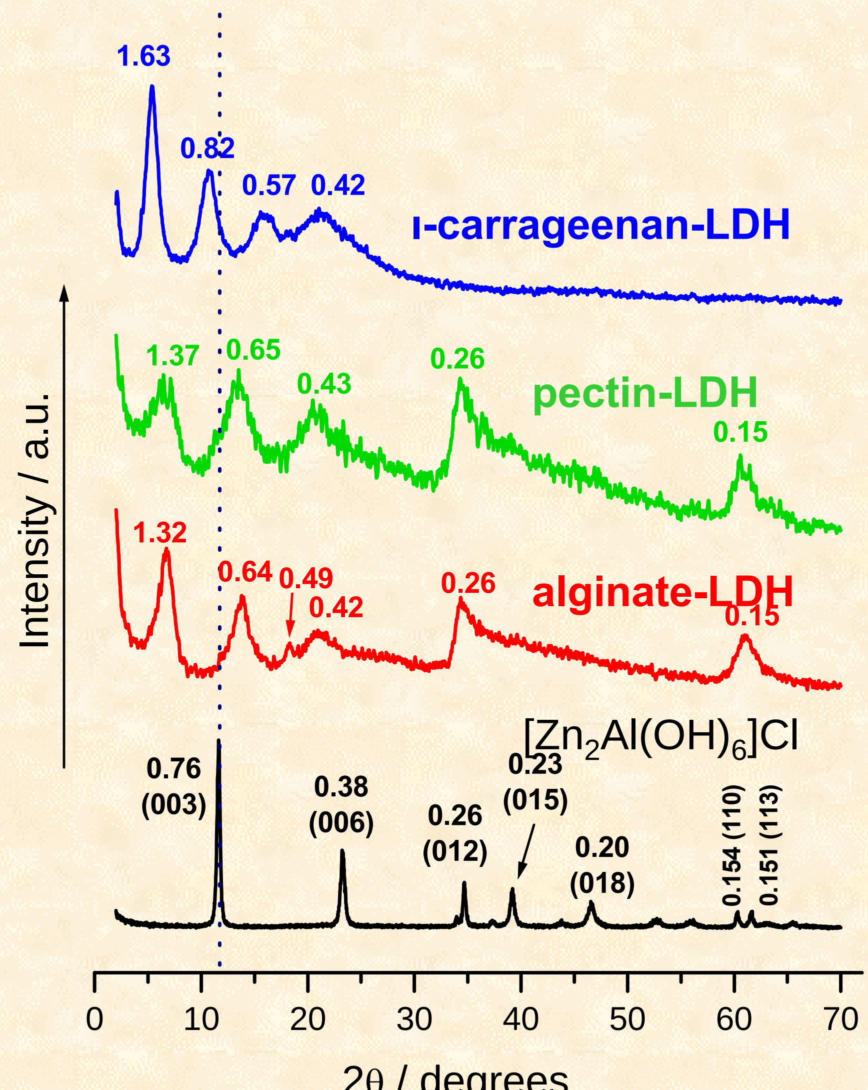
M. Darder, M. Lopez-Blanco, P. Aranda, F. Leroux, E. Ruiz-Hitzky Chem. Mater. 17, 1969-1977 (2005)

CHARACTERIZATION OF THE BIOPOLYMER- NANOCOMPOSITES

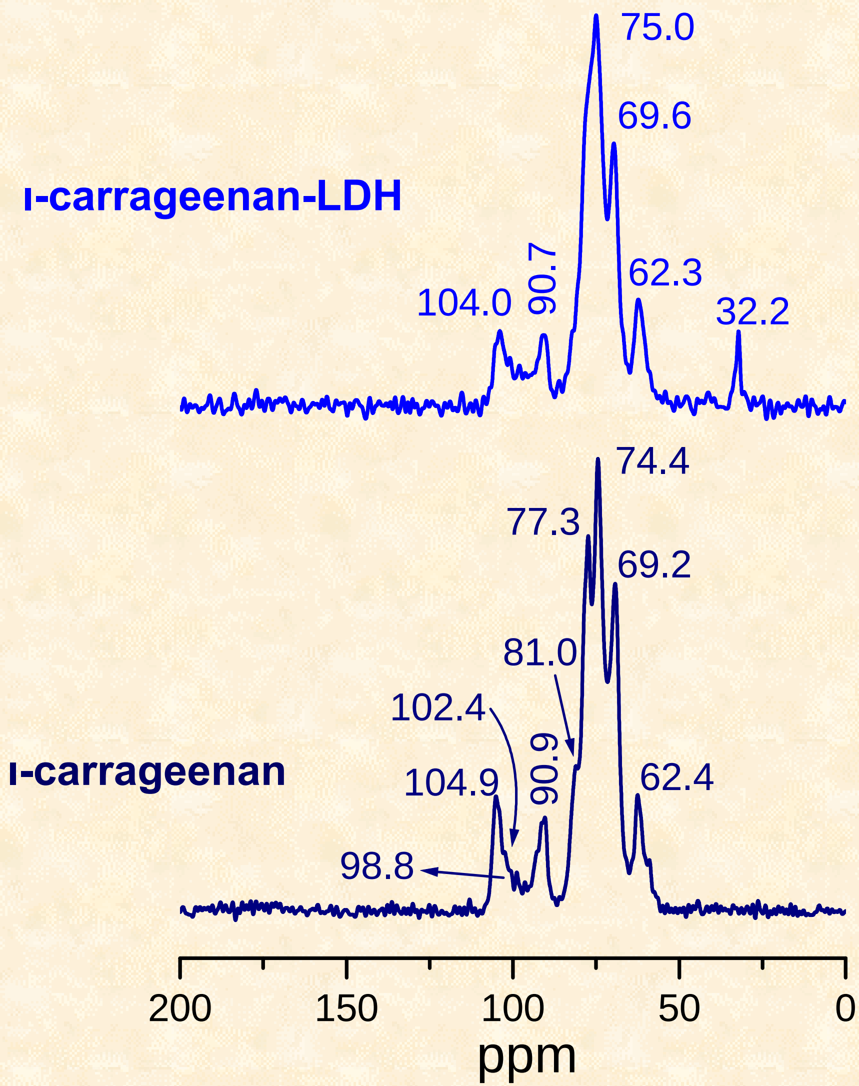
- X-ray diffraction
- FTIR spectroscopy
- Solid state ^{13}C NMR spectroscopy
- Scanning electron microscopy (SEM)
- Thermogravimetry (TG) and differential thermal analysis (DTA)
- Direct potentiometry

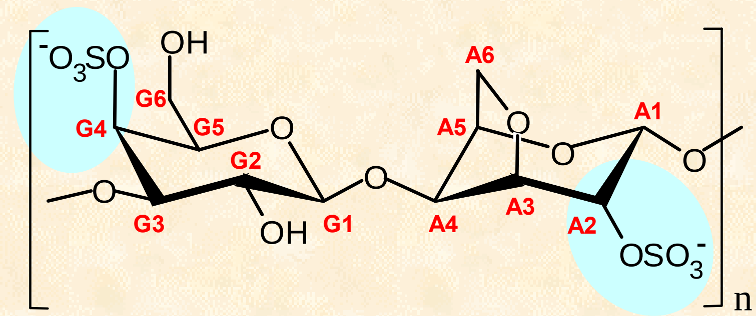
X-Ray Diffraction





Solid-state ^{13}C NMR spectroscopy





G4: 74.4 ppm ➔ 75.0 ppm

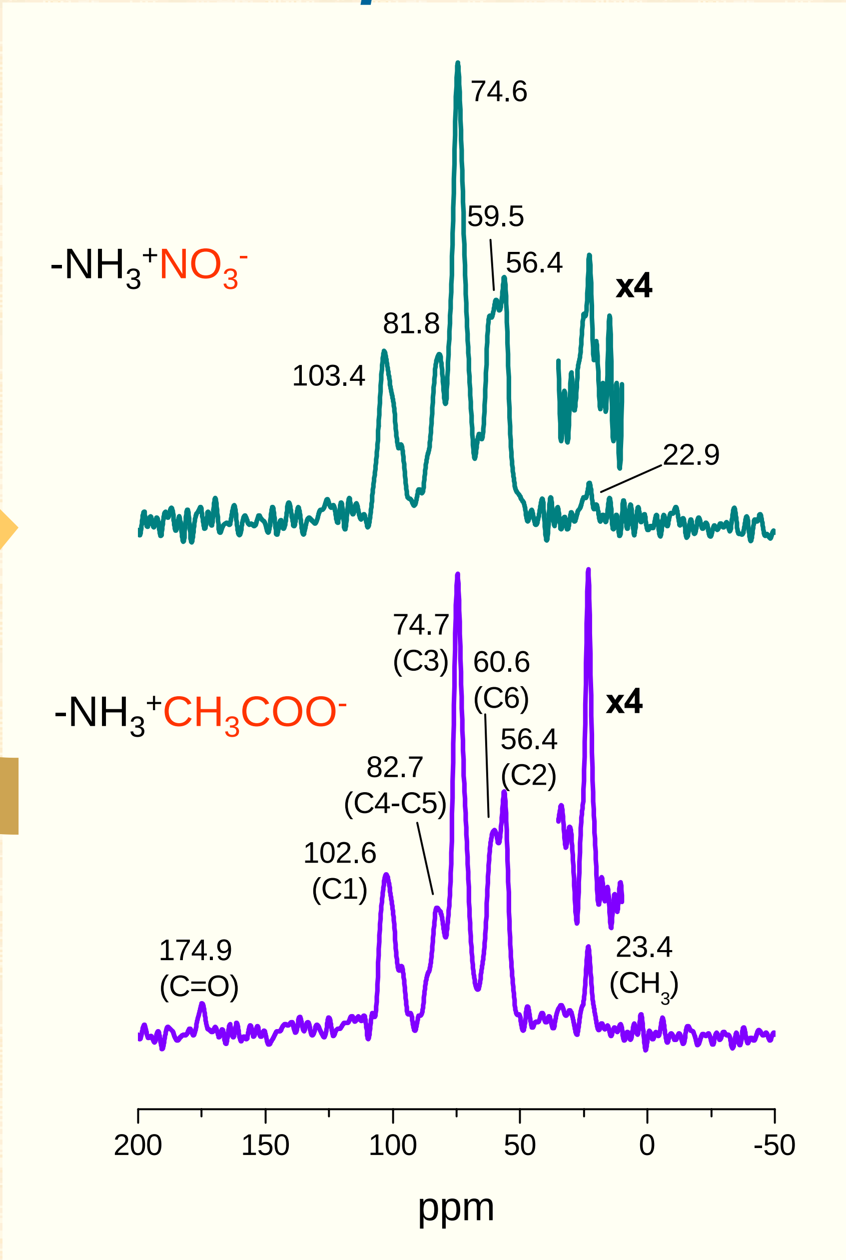
A2: 69.2 ppm ➔ 69.6 ppm

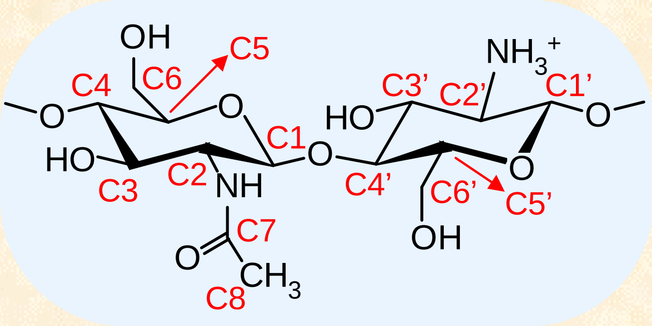
Chitosan-clay bio-nanocomposite

- **Anion-exchange behavior**

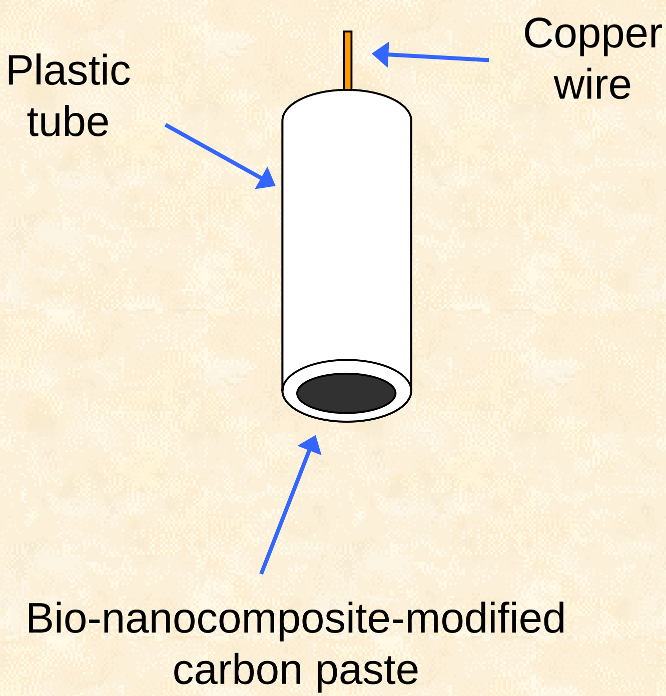
^{13}C NMR Spectroscopy

TREATMENT WITH $NaNO_3$

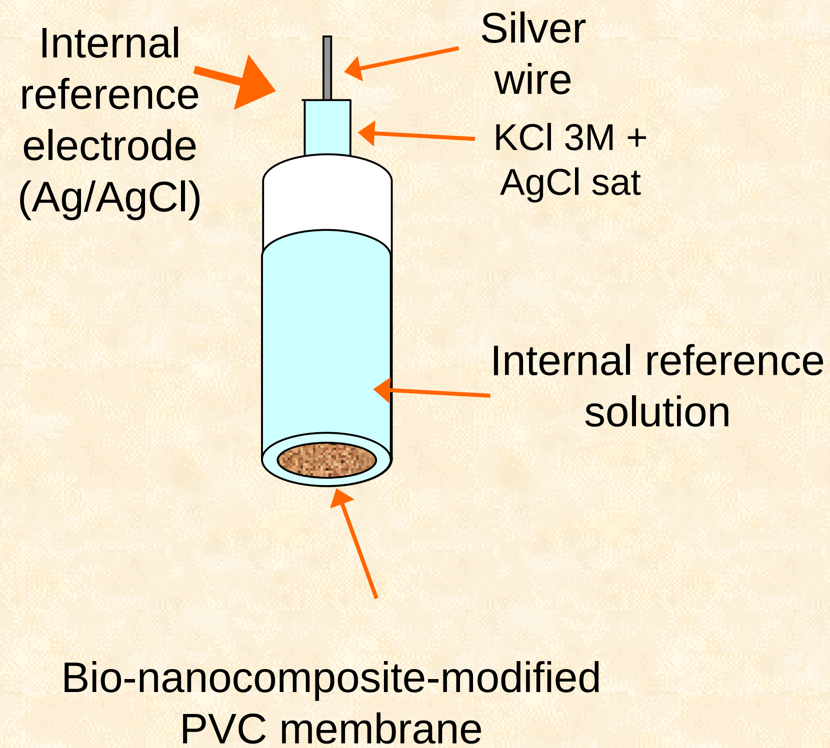




Development of potentiometric sensors

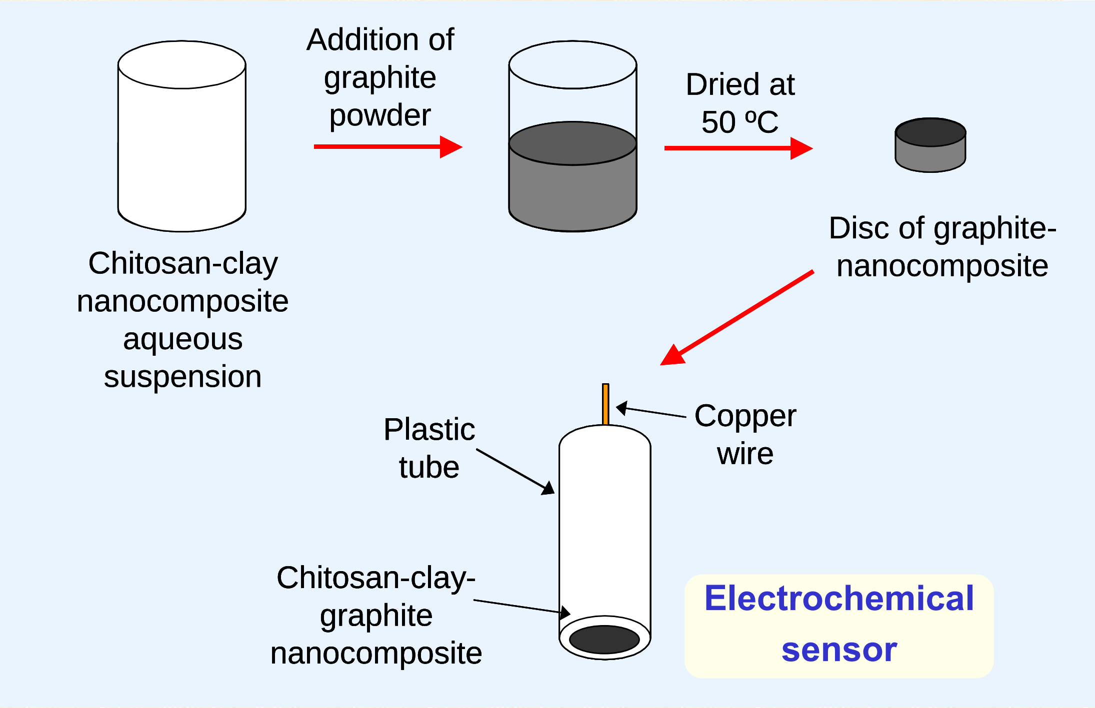


Carbon paste electrodes (CPEs)



PVC-membrane based electrodes

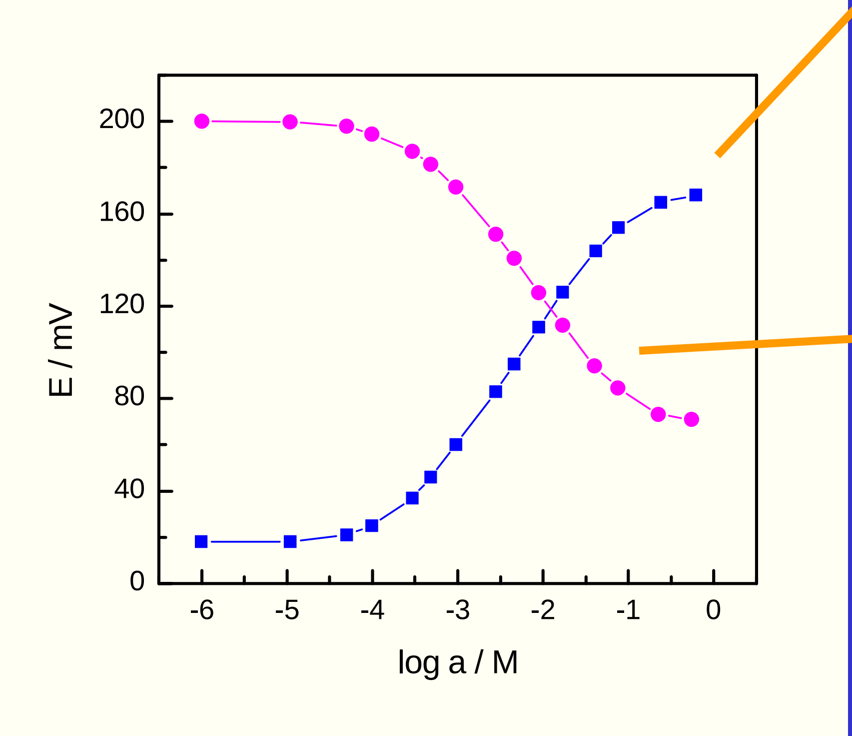
Chitosan-clay sensors development



The good mechanical properties of bio-nanocomposite avoid the use of binders as it is usual in CPEs or Epoxy Based Sensors

• **Potentiometric response**

Potentiometric measurement of NaCl with sensors prepared from different nanocomposites



Nanocomposite with a chitosan **monolayer**

Positive slope

Potentiometric response to **cations**

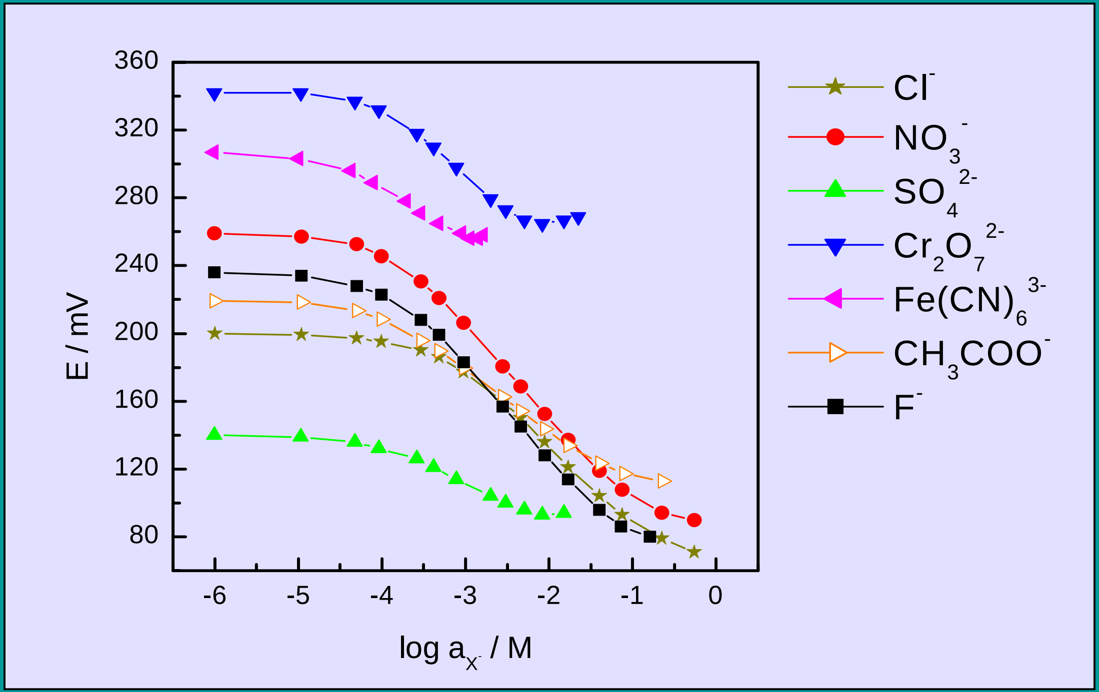
Nanocomposite with a chitosan **bilayer**

Negative slope

Potentiometric response to **anions**

Chitosan-montmorillonite potentiometric sensor

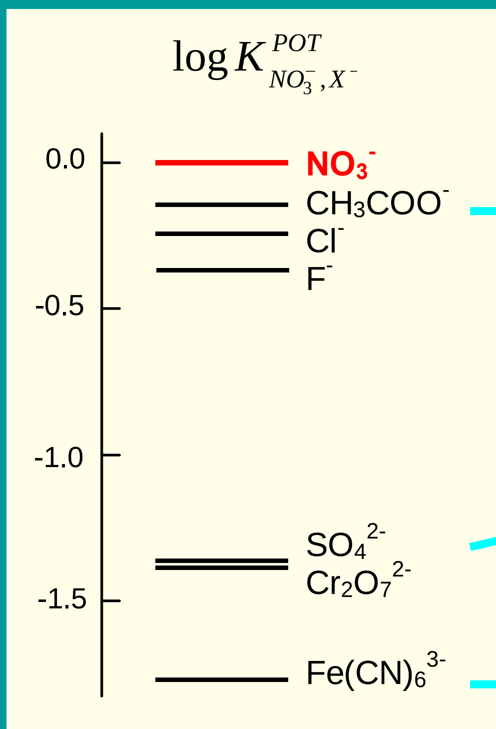
The potentiometric response of a sensor based on the chitosan-clay nanocomposite with a chitosan bilayer is evaluated towards different anions



M. DARDER, M. COLILLA, E. RUIZ-HITZKY *Chitosan-clay nanocomposites: application as electrochemical sensors* **Appl. Clay Sci. 28, 199-208 (2005)**

Selectivity coefficients

$$NO_3^- \approx CH_3COO^- \approx Cl^- >>> SO_4^{2-} \approx Cr_2O_7^{2-} >> Fe(CN)_6^{3-}$$

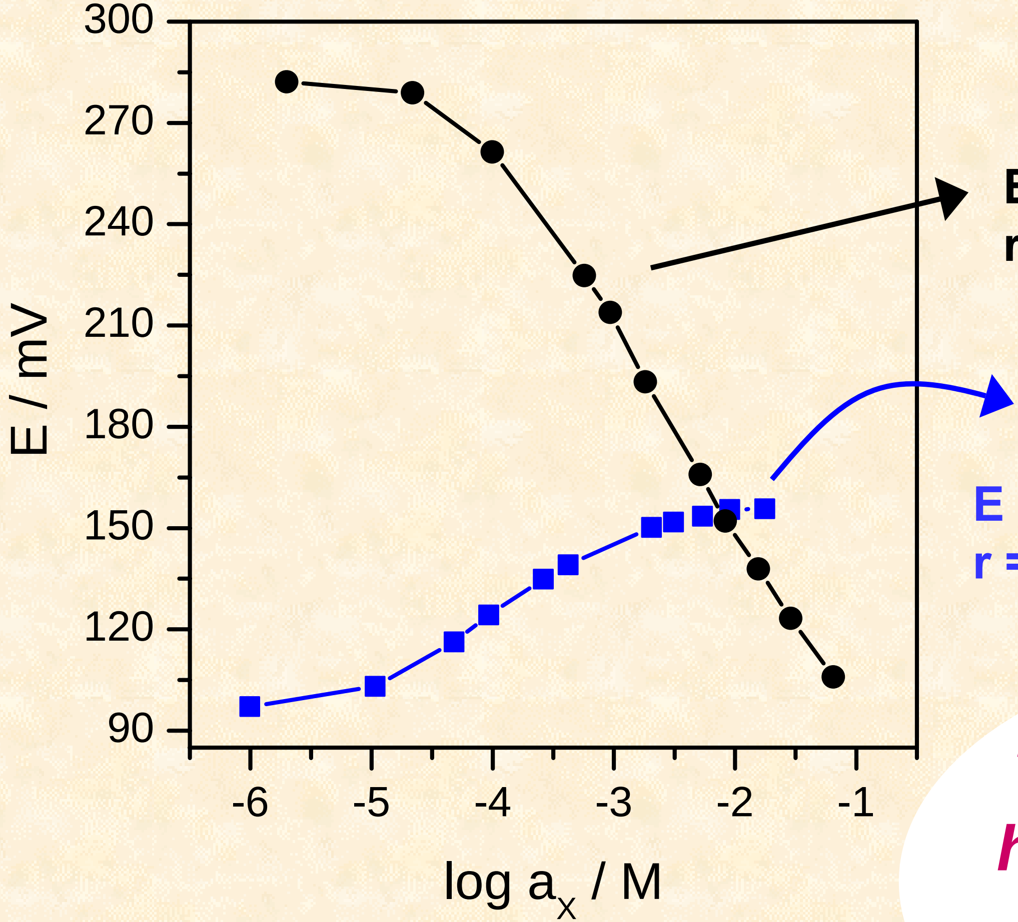


Partial selectivity to monovalent anions → **Cross-sensitivity**

The sensor is 25 times more selective for nitrate than divalent anions

The sensor is 60 times more selective for nitrate than trivalent anions

LDH Bio-nanocomposite CPEs



Zn_2Al/Cl LDH

$E = 35.9 - 57.3 \log a_{Cl^-}$

r = 0,9986

ι-carrageenan-LDH

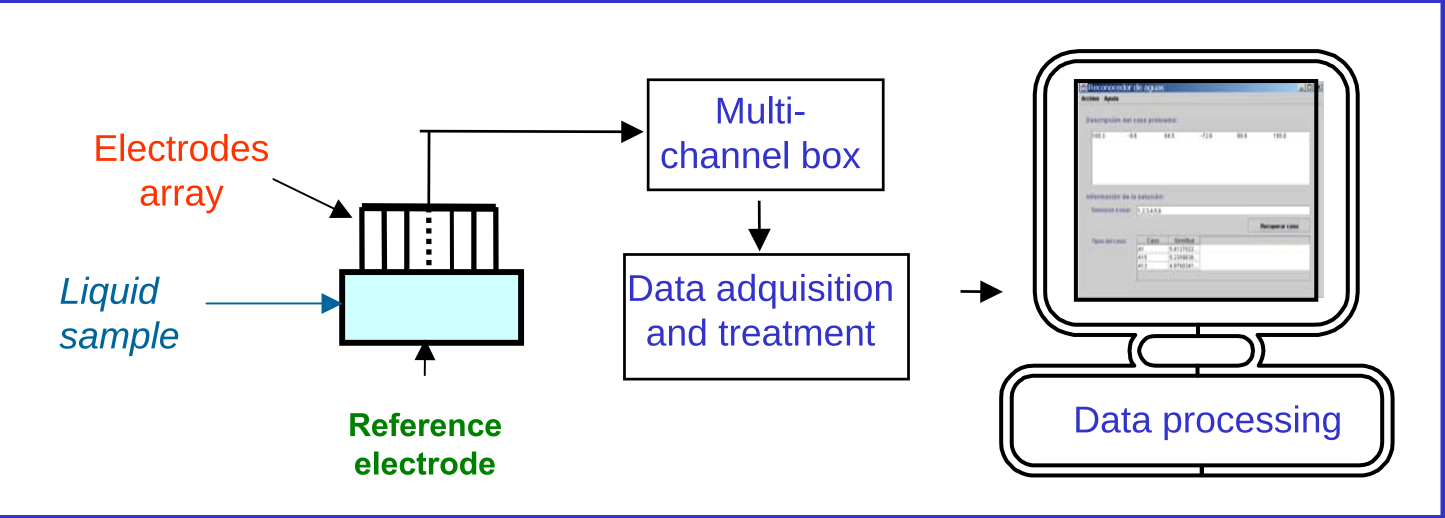
$E = 213.5 + 22.2 \log a_{Ca^{2+}}$

r = 0,998

The AEC of the LDH has been reversed to a CEC in the bionanocomposite

Sensor arrays controlled by Artificial Inteligence

Combination of sensors with AI techniques give sophisticated devices, as artificial noses and tongues



Application of Case-Based Reasoning (CBR) for multicomponent analysis

M. COLILLA, C.J. FERNÁNDEZ, E. RUIZ-HITZKY
<u>The Analyst</u>, 127, 1580-1582 (2002)

<u>Applications</u>

-water quality: drink water & industrial pollution

-Ions in biological fluids

-Automation in fertiirrigation

Home-made "electronic tongue" entirely developed in our lab, using sensors based on bio-nanocomposites, applied to control the water quality

CONCLUSIONS

Cationic or Anionic polysaccharides form bio-nanocomposites by combination at the nanometric scale with layered silicates (INTERCALATION) or double hydroxides (CO-ORGANISED ASSEMBLY) resulting in ***functional hybrid nanostructured materials*** *with:*

- *Good mechanical properties*
- *Controlled ion-exchange behaviour*

These results open a way to prepare novel bio-nanohybrids provided of structural or functional properties.

FUTURE WORK

The use of other layered host solids (phosphates, phosphonates, chalcogenides, etc.) & bio-polymers (polypeptides, nucleic acids, etc..)

Projects	Financed by
MAT2003-06003-C02-01	CICYT
07N / 0070 / 2002	Comunidad Autónoma de Madrid
IFAPA – 2002.000890	Junta de Andalucía