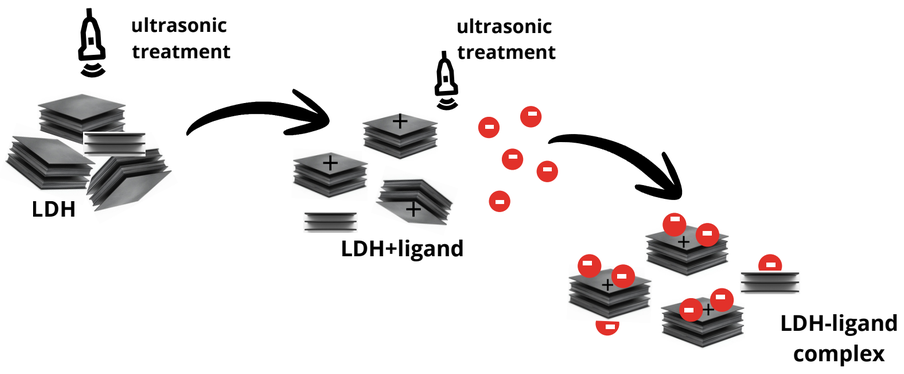
Surface Adsorption of Eosin Y on Carbonate-Intercalated Mg_2Al Layered Double Hydroxide



E. Dukhopelnikov[1], E. Bereznyak[1], A. Laguta[2], N. Hladkovska[1], Iu. Blyzniuk[1], A.N. Salak[3]

[1]O.Ya.Usikov Institute for Radiophysics and Electronics NASU, Ukraine

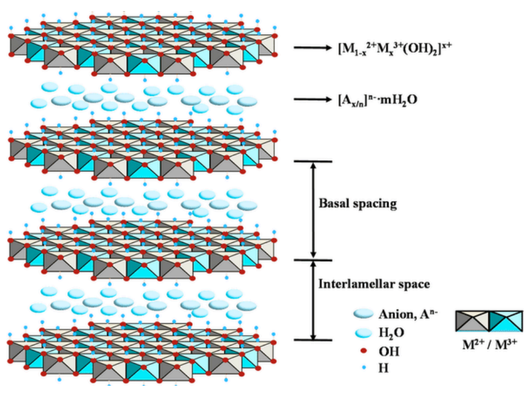
[2]V.N.Karazin Kharkiv National University, Ukraine

[3]DEMaC-CICECO-Aveiro Institute of Materials, University of Aveiro, Portugal

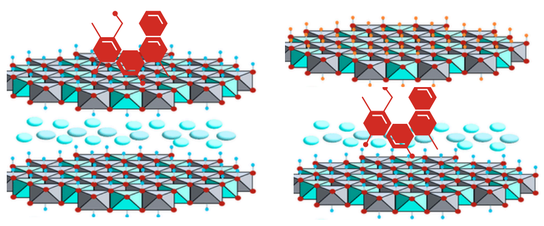
dukhopelnikov@gmail.com

LDH structure

Layered double hydroxides (LDH) have specific surface area of 2-D frames formed by positively charged mixed M^{2+}/M^{3+} metal hydroxide layers with anions in the interlayer.



Anionic dyes can interact with LDH nanoparticles through two mechanisms (surface adsorption and intercalation).



Aim

To obtain the spectroscopic markers of surface LDH adsorption complexes with dyes.

Objectives

- Determine the hydrodynamic and electrostatic characteristics of the EY-LDH complex in an aqueous suspension.
- Obtain the spectrum of EY adsorbed on the LDH surface.
- Calculate the encapsulation efficiency (EE, %) of EY on the LDH surface.

$$EE,\% = \frac{C_{lig} - C_{free}}{C_{lig}} \times 100$$

C_{lig} is total EY concentration
C_{free} is concentration of free EY

Experimental techniques

- Dynamic Light Scattering measurements
- Laser Doppler Electrophoresis measurements
- UV–Vis titration experiments

Reagents

LDH Mg_2AlCO_3

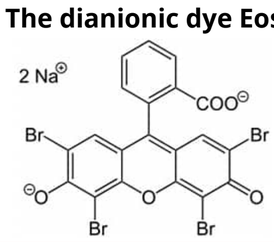
Mg^{2+} / Al^{3+}

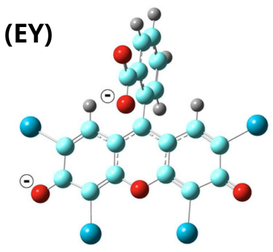
Anions, A^- CO_3^{2-}

Mg_2Al LDH with intercalated CO_3^{2-} anions has a reduced interlayer spacing and does not allow for the intercalation of bulky organic anions.

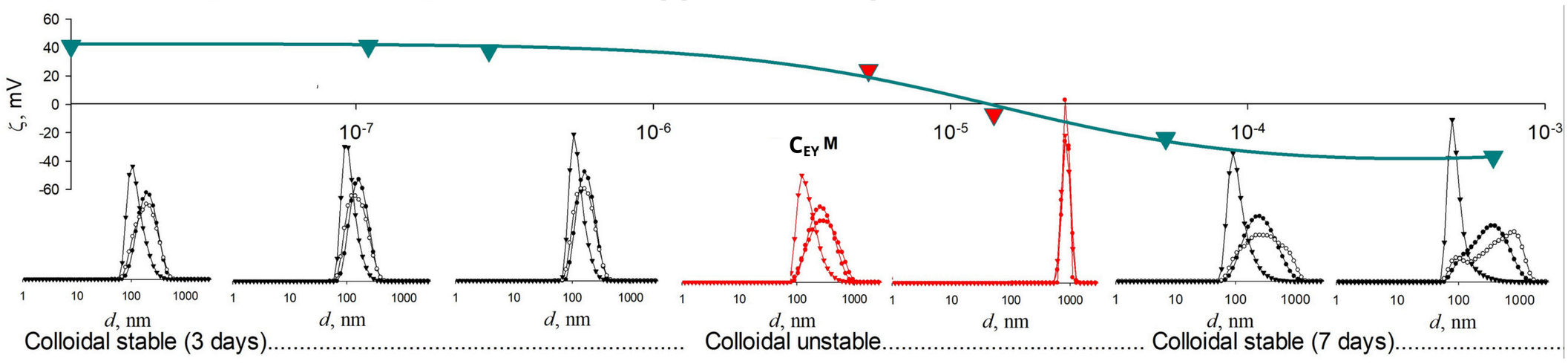
Ligand Eosin Y (EY)

The dianionic dye Eosin Y (EY)





Dynamic Light Scattering and Laser Doppler Electrophoresis results



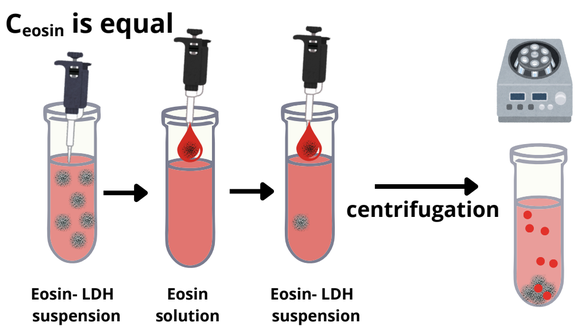
Dependency of zeta potential on EY concentration and size distribution by intensity, volume, and particle number

The dye-free LDH systems have low colloidal stability: the size and polydispersity index increase on day 3. EY affects the zeta potential primarily by adsorption. Overcharging leads to a colloidal stable system.

UV–Vis titration experiments

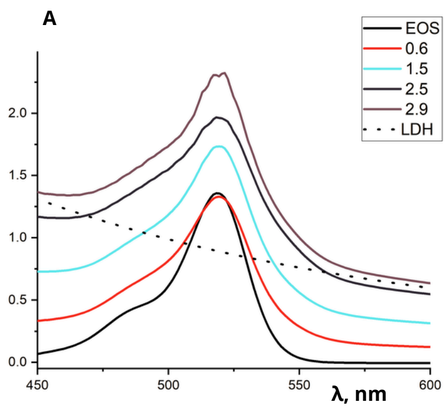
We used two different titration approaches to obtain spectra of EY - LDH suspensions and spectra of free eosin in the supernatant from centrifugation of these EY-LDH suspensions.

Scheme of titration experiment for EY - LDH suspensions with different LDH concentrations and their supernatants



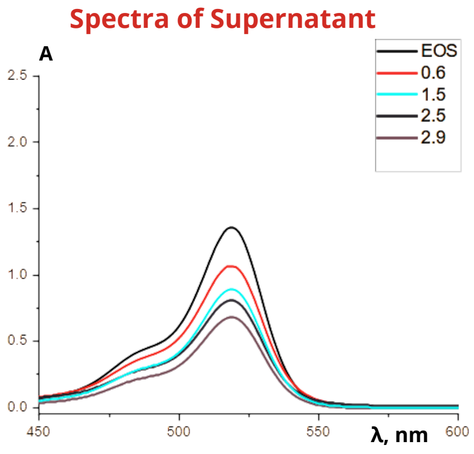
LDH sediment together with the bound dye, and allows the determination of the free EY concentration.

Spectra of Suspension



Titration spectra of EY - LDH suspensions demonstrate any significant shift of the EY absorption maximum.

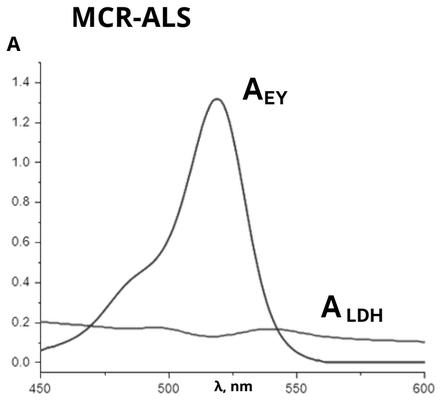
Spectra of Supernatant



Spectra of the supernatants of the centrifuged mixtures.

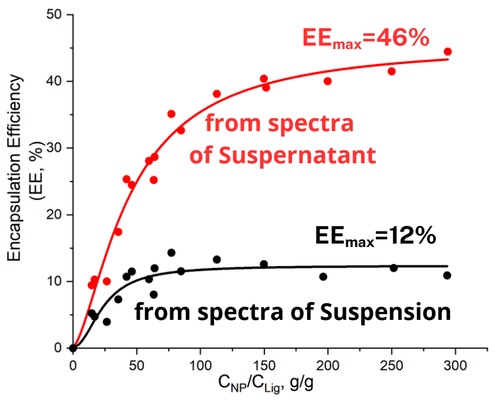
Analysis of titration data

MCR-ALS



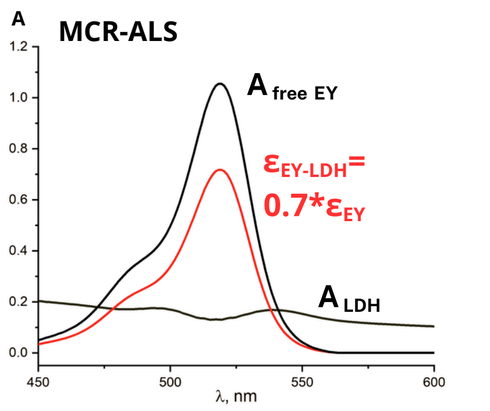
Spectral decomposition of suspension titration data by the MCR-ALS algorithm indicates only two absorbing species in the system, namely free EY and LDH particles.

The EE_{max} value obtained from the titration data of suspension spectra is very low (12%).



The maximum encapsulation efficiency of EY, which was calculated from the titration data of supernatant spectra, revealed a higher value (46%).

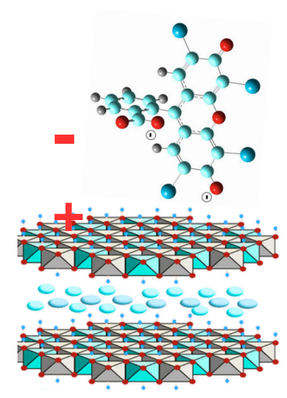
Analysis of differences in binding isotherms allowed us to obtain absorption spectra for the eosin-LDH system. Subsequent decomposition by the MCR-ALS algorithm revealed the presence of three absorbing species.



The adsorption of eosin is not accompanied by a shift in the spectrum of the dye but only leads to a decrease (by approximately 30%) in its extinction coefficient.

Conclusions

Eosin Y adsorbed on the Mg_2AlCO_3 surface



ζ-potential = -40 mV

EE_{max}=46%

$\varepsilon_{EY\text{-}LDH}$=0.7$\varepsilon_{eos}$*

Surface adsorption of Eosin Y on Mg_2Al–CO_3 LDH changes the particle surface charge from +40 mV to -40 mV.

The spectrum of EY bound to the LDH surface does not shift but has a lower intensity (by 30%).

The encapsulation efficiency of EY on the Mg_2AlCO_3 surface is not high (EE_{max}=46%).