Zeolites – nanostructered materials for adsorption, catalysis and desinfection

Prof. Nevenka Rajić
Faculty of Technology and Metallurgy,
University of Belgrade, SERBIE

NOWELTIES: September, 2020, 16-18, Zagreb

Outlines

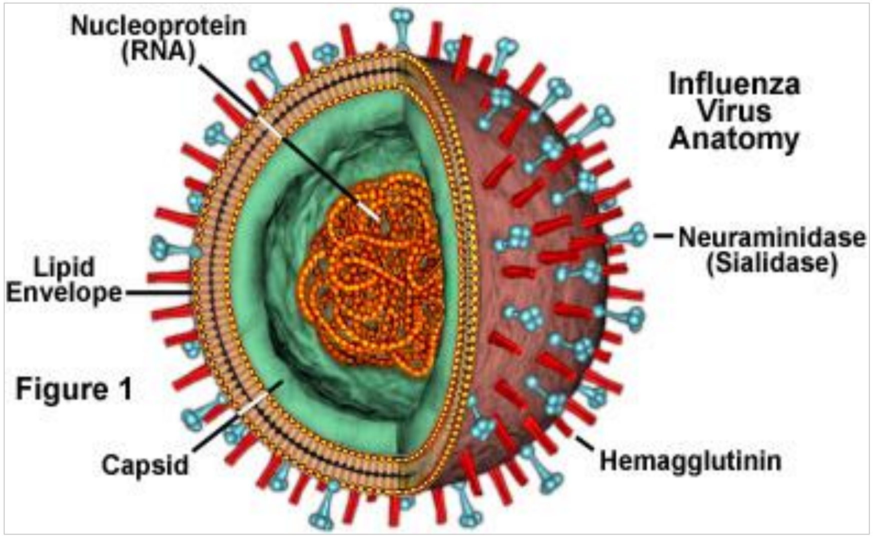
- Nanostructured solids - definition
- Nanoporous materials – division
- Zeolites – microporous materials
- Basic methods for zeolite characterization
- Adsorption experiment
- Adsorption isotherms, kinetics and thermodynamics
- Catalytic and antimicrobial activity

- **Nanostructure** is a structure with at least one dimension 1-100 nm
- It is essential to obtain particles or pores with uniform diameters and shapes, and for particular application to arrange and insert them in a superstructure.
- Perform special optical, electronic, magnetic, and chemical properties.
- Aapplications in different areas such as signal transmission, data and energy storage, **pollutant removal**, catalysis, biology, etc.

Nanostructured biological structures

2 nm diameter

DNA:
http://www.biojobblog.com/uploads/image/dna_500.jpg



~50 – 100 nm diameter

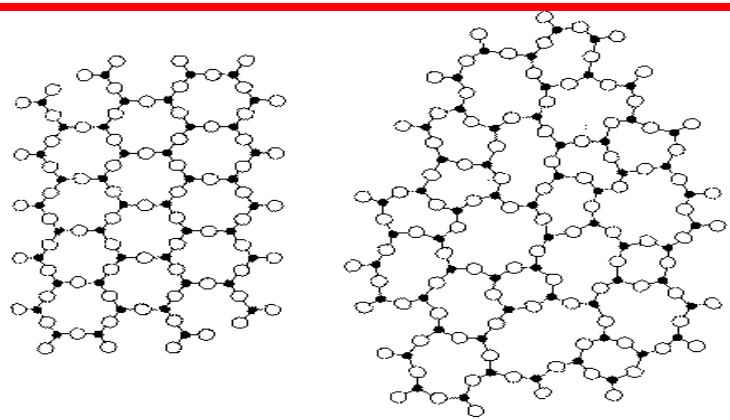
Flu virus:
http://www.chm.bris.ac.uk/webprojects2006/Kelly/influenzafigure1.jpg

Crystalline vs. Amorphous solids

- **Crystalline solid:** a solid whose constituents (atoms, molecules, or ions) are arranged in an orderly, repeating pattern extending in all three spatial dimensions.

- **Crystals:**
  Short-range order
  Long-range order

- **Amorphous solids:**
  ~Short-range order
  No Long-range order

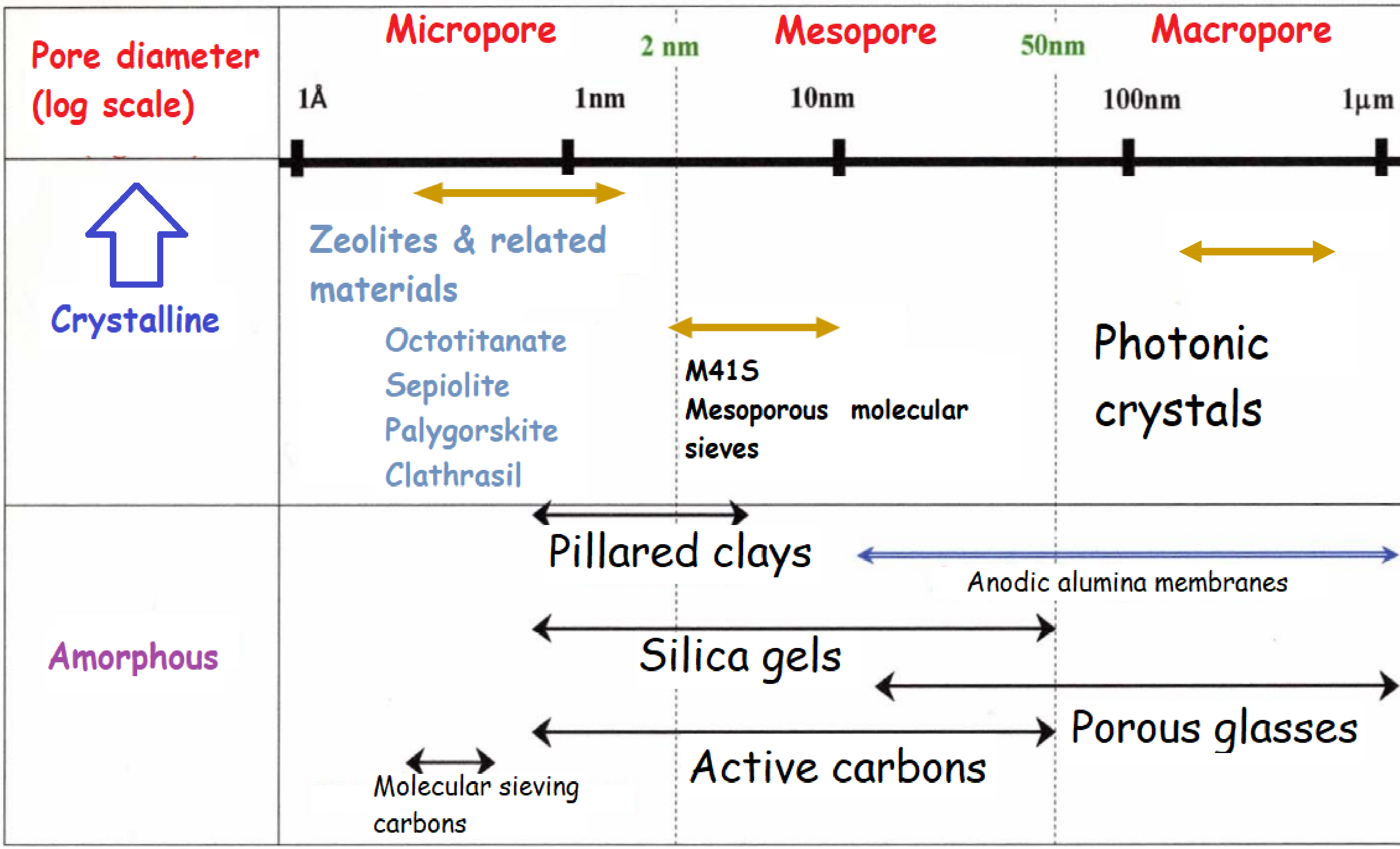


Nanoporous materials

- **IUPAC** (International Union of Pure and Applied Chemistry):

- microporous, $d < 2$ nm
- mesoporous, $2 \text{ nm} < d < 50$ nm
- macroporous, $d > 50$ nm

Pore size distribution of different materials



Zeolites - extraordinary minerals!

Crystalline 3D-aluminosilicates with open structures;
Exhibit unique properties:

Molecular sieve - separate gases based on molecular size,
Ion exchange – pick up ions from water media and immobilizied them,
Adsorption – immobilize different species onto and into their interior
Catalytic – possess Brönsted and Lewis acid sites important for acid-base catalysis.

Zeolite structure

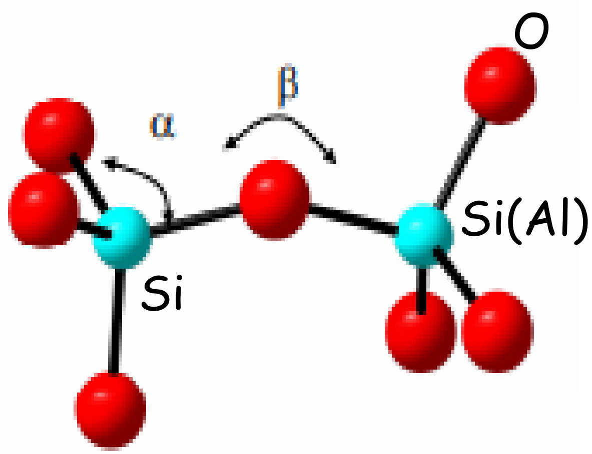
- Based on a rigid anionic framework with well-defined **channels** running through them that intersect at cavities.

- **Cavities** contain exchangeable metal cations (Na^+, K^+, etc.)

- "Boiling stone": zeolites lose water on heating.

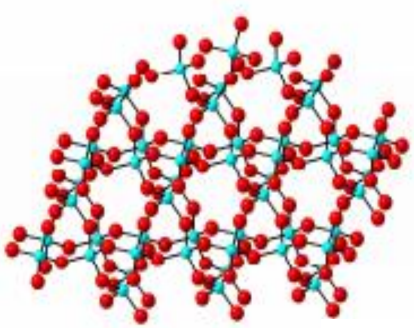
- Cavity size is from 200 to 2000 pm, therefore zeolites are classified as microporous substances.

- **$M_{x/n}[(AlO_2)_x (SiO_2)_y]\ mH_2O$**, where cations **M** of valence **n** neutralize the negative change on the framework.

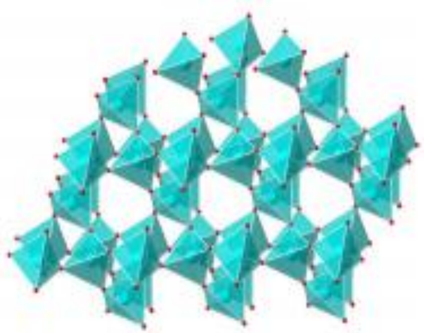


The primary building blocks of zeolites are corner-shared $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedra.

•flexible Si/Al-O-Si/Al linkage (120-180°)



quartz

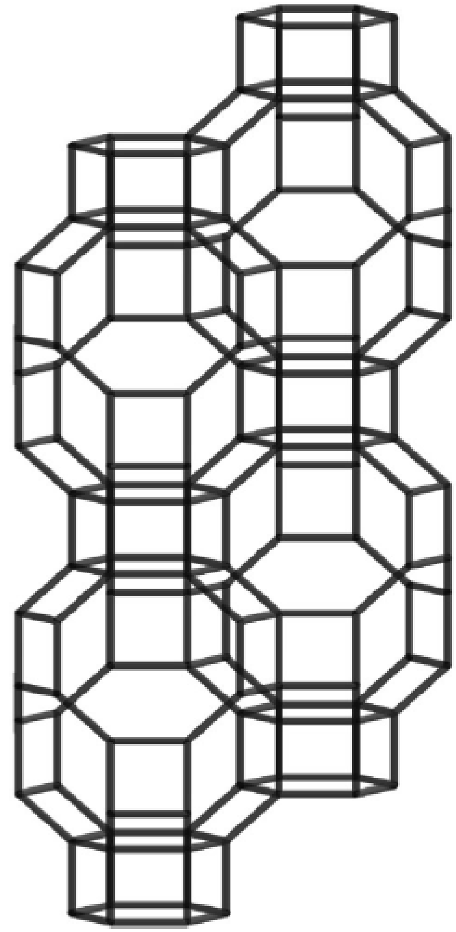


•Can link by 2, 3 or 4 corners, forming a wide variety of structures.

Channels and cavities

Channels may be parallel to:

- a single direction, resulting in fibrous crystals
- two directions - lamellar crys.
- three directions (e.g. cubic axes) - strong bonding occurs in three directions.



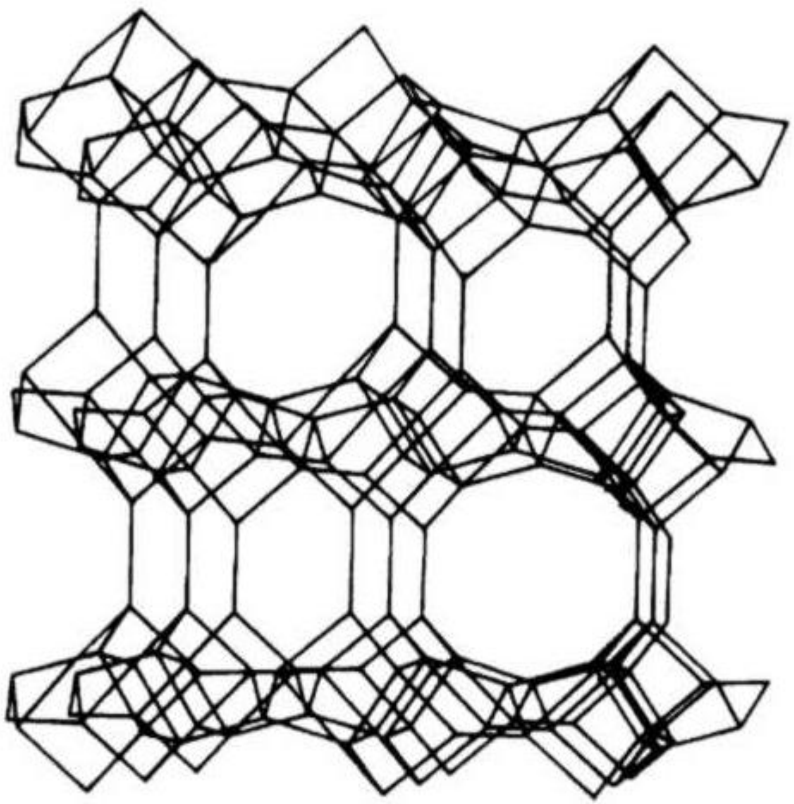
"Chabazite cage" a main feature of the **CHA** structure (0.67 nm x 1.0 nm)

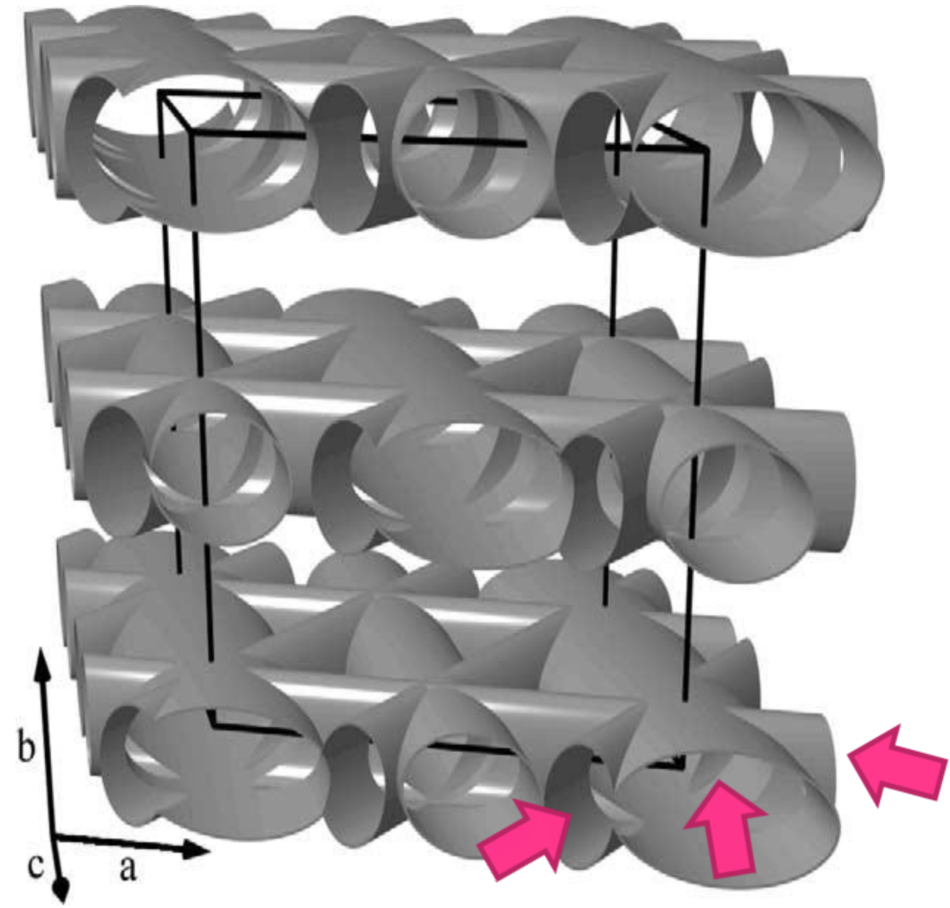
Natural zeolites

In the past most efforts were devoted to synthetic zeolites (more than 150 different structure type);

In recent years an increasing attention has been directed towards natural zeolites, whose status changed from that of a museum curiosity to an important mineral commodity.

Clinoptilolite



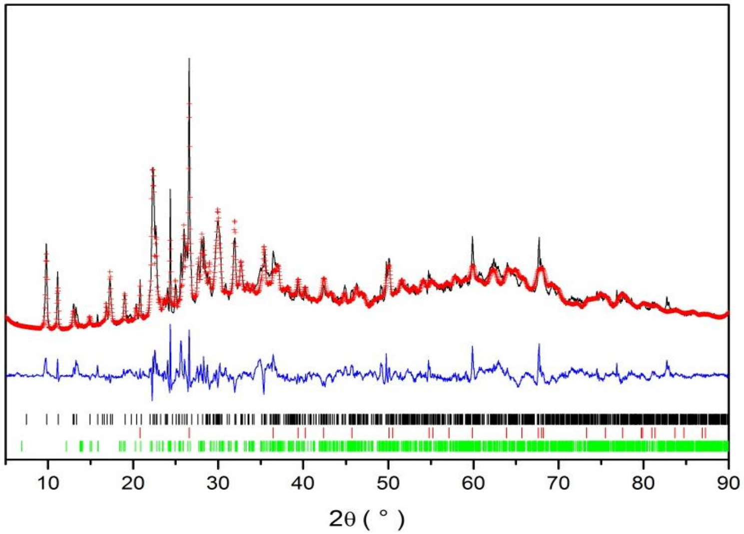


Clinoptilolite lattice: Three dimensional system of channels

Characterization of a zeolite-based adsorbent

- Zeolite content in a tuff (Rietveld analysis)
- Elemental analysis of the zeolite phase (EDS)
- Textural properties (BET)
- Cation exchange capacity (CEC)

1. Mineral composition



A quantitative XRPD analysis of the tuff sample gives mineral contents.

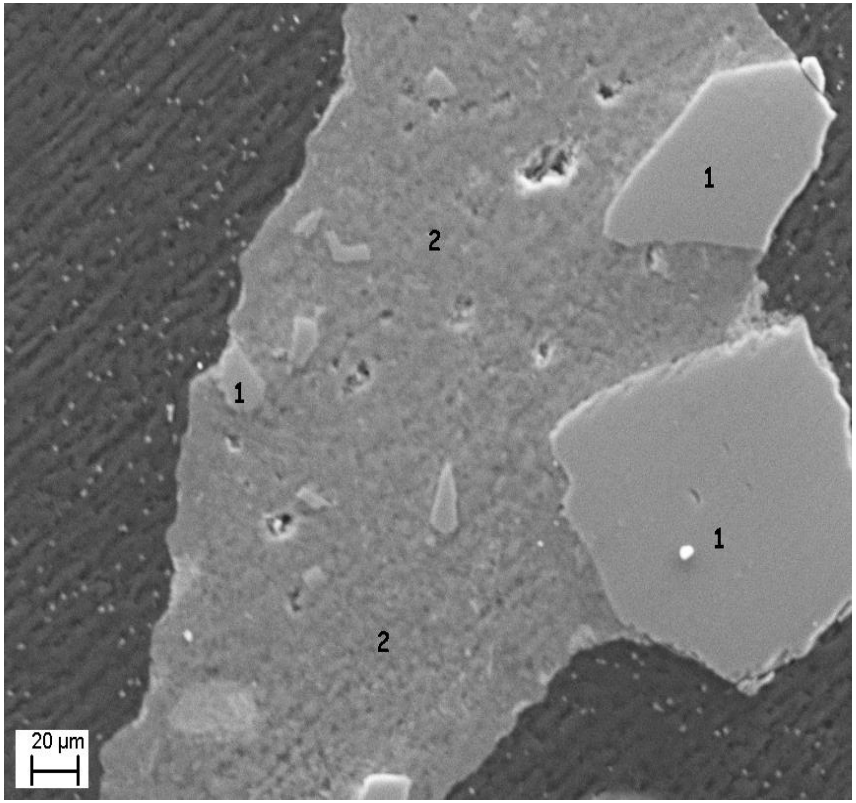
- Clinoptilolite (75-85 wt.%)
- Feldspars (10-15 wt.%)
- Quartz (8-10 wt.%)

N. Rajic et al, J. Hazard Mater. 172 (2009) 1450-1457.

2. Elemental analysis of clinoptilolite phase

Elemental analysis can be obtained by EDXS.

In clinoptilolite phase the Si/Al molar ratio is in the range 4.7-5.

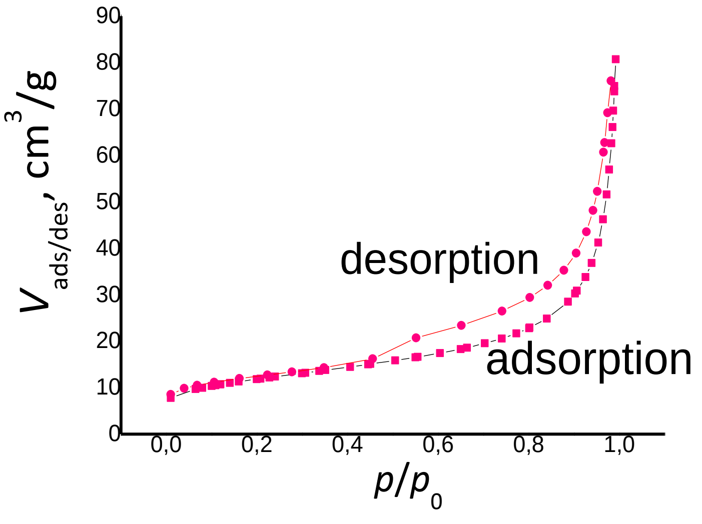


1 – feldspar (Si/Al molar ratio <3)

2 - clinoptilolite

N. Rajic et al, J. Hazard Mater. 172 (2009) 1450-1457

3. Textural properties



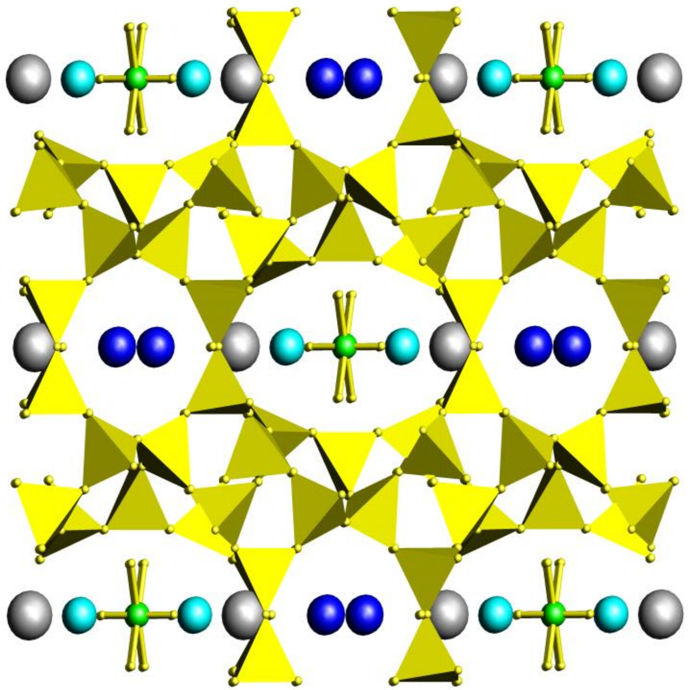
S_{BET}, $m^2\ g^{-1}$	42
S_{meso}, $m^2\ g^{-1}$	32
V_{mic}, $cm^3\ g^{-1}$	0.0052
A_L, $m^2\ g^{-1}$	57

N_2 adsorption/desorption isotherms at -196 °C

S_{BET} – calculated by BET method;
V_{mic}- micropore volume;
S_{meso} - mesoporous surface area calculated using the αS-plot method;
A_L - surface area from Langmuir method.

S Jevtić et al., Micropor Mesopor Mater 197 (2014) 92-100

4. Cation exchange capacity (CEC)



CEC – 150-200 mmolM^+/100 g

$Z(s) + NH_4^+(aq) \rightleftarrows NH_4\text{-}Z(s) + M^{n+}(aq)$

$Ca_{1.6}Mg_{0.7}K_{0.7}Na_{0.3}Al_{5.5}Si_{26}O_{72}\cdot 23H_2O$

Why adsorption is chosen?

- It has advantages over the other methods because of simple design and can involve low investment considering of both cost and land required,
- This process is widely used for treatment of industrial wastewater from inorganic and organic pollutants being in line of principles of **Green Chemistry**.

What is Adsorption?

- Adsorption is the transfer of a material from liquid (or gaseous phase) to a solid surface.
- The substance that is transferred to the surface is the **adsorbate**.
- The solid on which the adsorbate deposits is the **adsorbent.**

Adsorbent Example: Silica gel, Activated carbon, Alumina, Zeolites and molecular sieves, Polymers.

Factors affecting the adsorption

- The physical and chemical properties of the **adsorbate**.
- The temperature at which the process occurs.
- The properties of the **adsorbent**.
- The adsorption isotherm or equilibrium adsorption data.

Physical and chemical adsorption

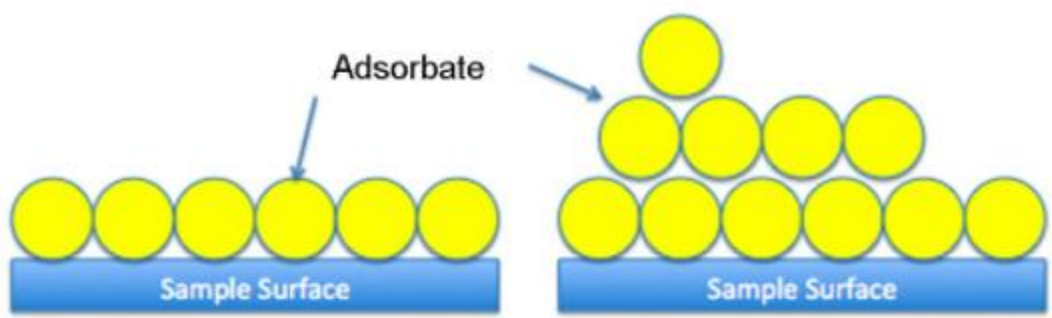
- Physical adsorption occurs when the bonding forces are dispersion and/or coulombic type (reversible).

- Chemical adsorption occurs when there is sharing of electrons between adsorbent and adsorbate (irreversible).
    - The amount of heat released during this process is equal to the heat of reaction.

Types of Adsorption

- Single component
- Multicomponent

Single component: The heat of adsorption of the first monolayer is much tronger than the heat of adsorption of the second (and all following) layers.



Single-component: Monolayer models

Two following isotherms are more commonly used:

- Langmuir
- Fraundlich

as well as the combination of L&F - Sips isotherm

1. The Langmuir model

- The model is based on:
  1) each surface site is singly occupied,
- 2) there is no interaction between the adsorbed species,
- 3) adsorption enthalpy is independent on surface coverage,
- 4) adsorption energy is constant thus creating homogeneity of energy on the surface

$$q_e = \frac{q_{max} b_L C_e}{1 + b_L C_e}$$

$$q_e = \frac{q_{\max} b_L C_e}{1 + b_L C_e}$$

- C_e is the equilibrium concentration of the solute (mg dm^{-3})
- q_e is the equilibrium concentration of the solute adsorbed (mg g^{-1})
- q_{max} (mg g^{-1}) is the maximum achievable uptake by a system
- b_L (dm^3 mg^{-1}) is related to the affinity between the sorbate and the sorbent: unfavourable (> 1) , favourable ($0<b_L< 1$) and irreversible (=0) .

2. The Freundlich model

- Based on:

1) lateral interactions between adsorbate species,

2) energetic surface heterogeneity.

$$\log q_e = \log K_f + \frac{1}{n}\log C_e$$

$$\log q_e = \log K_f + \frac{1}{n}\log C_e$$

C_e - equilibrium concentration of solute (mg dm^{-3}),

q_e - equilibrium concentration of the solute adsorbed (mg g^{-1})

K_f (dm^3 g^{-1}) and *n* (dimensionless) - constants that are indicators of the adsorption capacity and adsorption intensity, respectively.

Sips model

Suitable for predicting adsorption on heterogeneous surfaces, thus avoiding the limitation of increased adsorbate concentration normally associated with the Freundlich model.

At **low adsorbate concentration** the Sips model reduces to the Freundlich model,

At **high concentration** of adsorbate, it predicts the Langmuir model (monolayer adsorption).

3. Sips model

$$q_e = \frac{q_{max}(b_S C_e)^{n_S}}{1+(b_S C_e)^{n_S}}$$

b_s, n_s - Sips constants

Adsorption experiments for Zn(II) removal

- **Batch experiments**
- Grain size: 0.063-0.1 mm
- Initial conc.:

  100-400 mg TM dm^{-3}

  (TM – Mn, Ni, Cu, Zn, Pb)
- Thermostatic bath:

  25-55 °C

- ❑ Adsorption isotherms
- ❑ Kinetic studies
  - kinetic models
  - diffusion effects
- ❑ Thermodynamic study

Parameters obtained by the two adsorption isotherm equations

T (K)	Sips isotherm				Langmuir isotherm		
	q_{max} (mg g^{-1})	b_S (dm^3 mg^{-1})	n_S	R^2	q_{max} (mg g^{-1})	b_L (dm^3 mg^{-1})	R^2
298	170	3.41×10^{-7}	0.301	0.999	12.0	0.0184	0.930
308	22.6	0.00636	0.560	0.996	15.5	0.0198	0.971
318	19.5	0.0221	0.603	0.999	15.8	0.0373	0.977
328	21.7	0.0150	0.576	0.999	16.6	0.0319	0.974
338	17.5	0.0441	0.857	0.995	16.8	0.0468	0.992

***R*²** - the correlation coefficient

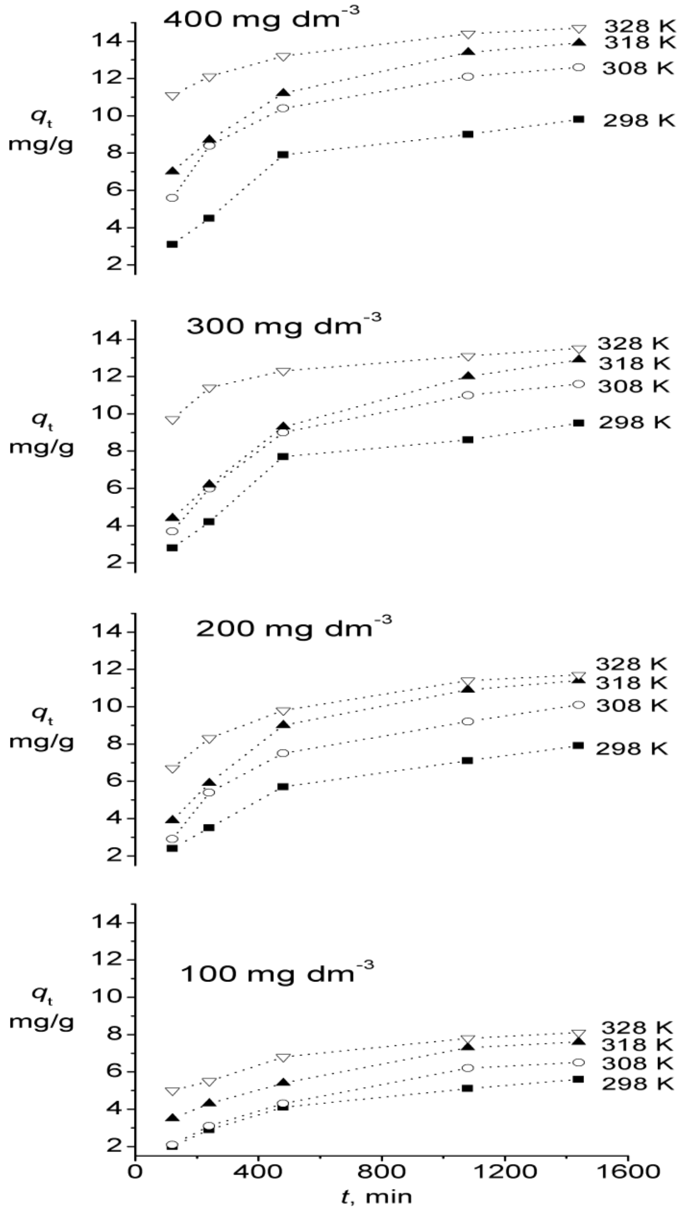
- R^2 values show that the Sips model better describes the Zn(II) adsorption on zeolite

- **Notice:** The Langmuir isotherm describes adsorption on highly homogenous surfaces and is not suitable for adsorption on minerals because of irregularities on their surface.
- The Langmuir-Freundlich (Sips) isotherm contains the heterogeneity factor (n_s) by which the affinity of the adsorbing surface is taken into account.

Kinetic analysis

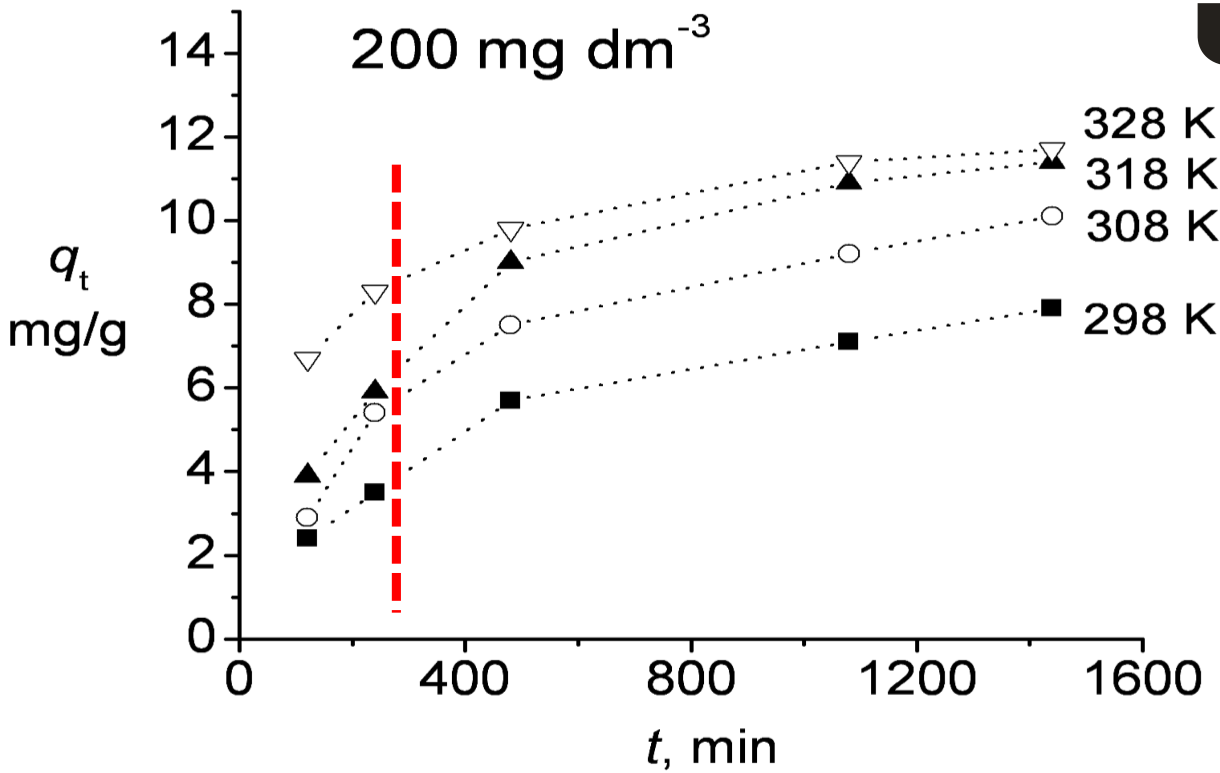
- The adsorption dependence on time should be investigated at different temperatures and initial adsorbate concentrations:
- Temperature: 298, 308, 318 and 328 K and
- *Initial solute conc:* C_0 = 100, 200, 300 and 400 mg Zn dm^{-3}.

Ink1



Zn(II) adsorption kinetics for different initial Zn(II) concs.;

q_t - conc. of the adsorbed Zn(II) (mg per 1 g of zeolite after time t.



The Zn(II) uptake increases rather sharply for the first 1 h (especially at higher temperatures). Than the adsorption proceeds more gradually.

The data from the figure were analyzed using two reaction-based kinetic models, and a diffusion-based model (Weber-Morris).

The Lagergren's models:

1. The first-order model.
2. The second-order model.

- The first model is given by the equation:

$$\frac{dq_t}{dt} = k_1(q_e - q_t)$$

- q_e (mg g^{-1}) is the adsorption capacity at equilibrium
- k_1 (min^{-1}) is the rate constant of the first-order adsorption

- The second reaction-based model is based on the following pseudo-second-order rate equation:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2$$

Integration yields:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$

- The plot of t/q_t vs t will give a straight line if the experimental data conform to this kinetic model.
- q_e and k_2 are obtained, respectively, from the slope and intercept of such a plot.

C_0 (mg Zn dm^{-3})	T (K)	Lagergren's first-order rate constants		Pseudo-second-order rate parameters		
		k_1 (min^{-1})	R^2	k_2 (g mg^{-1} min^{-1})	q_e (mg g^{-1})	R^2
100	298	2.04×10^{-3}	0.995	5.00×10^{-4}	6.67	0.998
	308	2.83×10^{-3}	0.985	3.06×10^{-4}	8.30	0.996
	318	2.76×10^{-3}	0.980	4.77×10^{-4}	8.81	0.994
	328	2.49×10^{-3}	0.998	9.54×10^{-4}	8.71	0.999
200	298	2.02×10^{-3}	0.987	2.50×10^{-4}	9.98	0.995
	308	2.09×10^{-3}	0.983	2.30×10^{-4}	12.5	0.996
	318	2.83×10^{-3}	0.997	2.41×10^{-4}	13.87	0.998
	328	2.92×10^{-3}	0.998	6.44×10^{-4}	12.7	0.999
300	298	2.10×10^{-3}	0.909	2.20×10^{-4}	12.0	0.985
	308	2.67×10^{-3}	0.996	2.18×10^{-4}	14.3	0.998
	318	2.35×10^{-3}	0.994	1.83×10^{-4}	15.9	0.998
	328	2.21×10^{-3}	0.969	12.5×10^{-4}	13.9	0.999
400	298	2.23×10^{-3}	0.941	2.37×10^{-4}	12.1	0.990
	308	2.67×10^{-3}	0.993	4.11×10^{-4}	14.1	0.999
	318	2.76×10^{-3}	0.996	3.77×10^{-4}	15.5	0.999
	328	2.58×10^{-3}	0.999	11.1×10^{-4}	15.2	0.999

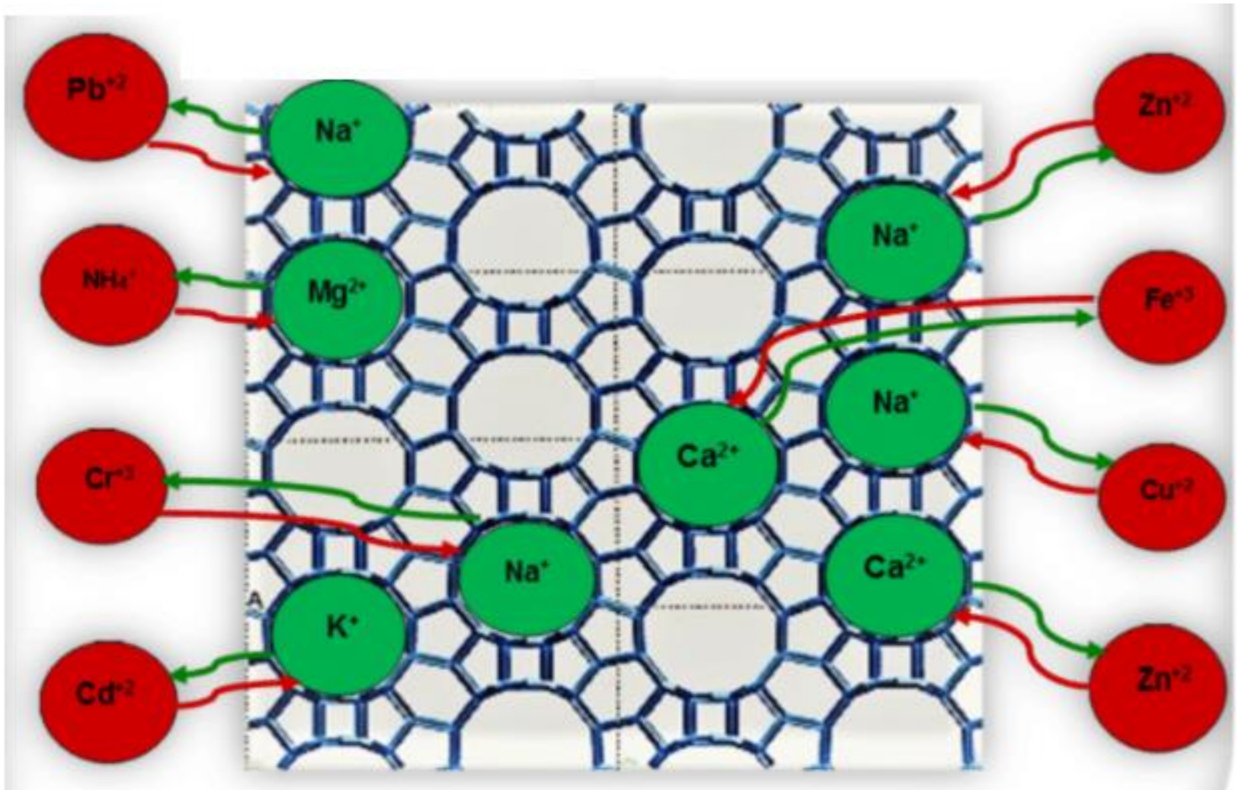
Discussion

The pseudo-second-order model gives a slightly better description of the Zn(II) adsorption kinetics as judged by the R^2 values.

The k_1 and k_2 rate constants for the Lagergren's models, change rather **irregularly** with temperature for all initial Zn(II) concentrations!

At least two factors could be the cause (next slide).

Diffusional effects



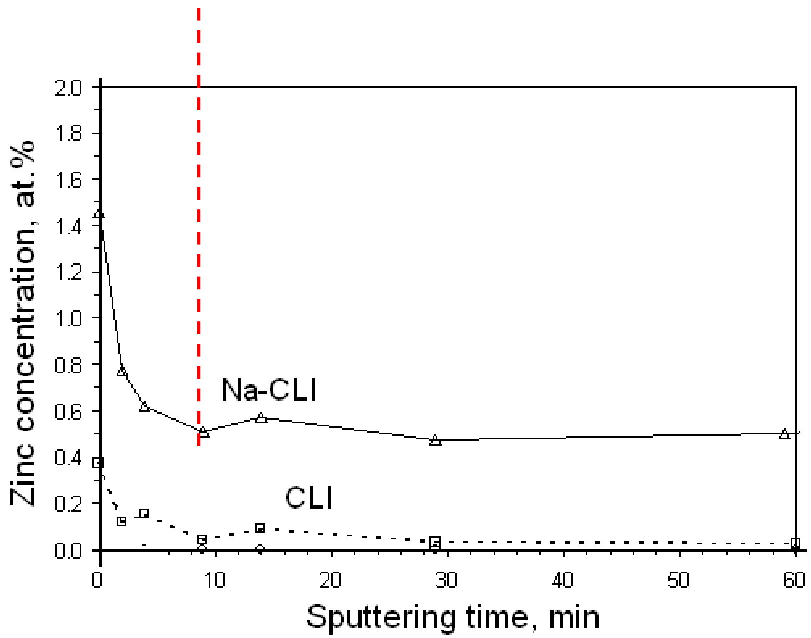
$$Zn^{2+}(aq) + M\text{-}Z(s) \rightleftarrows Zn\text{-}Z(s) + 2M^{+}(aq)$$

1) In the ion-exchnge reaction diffusional process **is necessary to be taken into account**.

2) Zn(II) ion is not present in soolution only as the hydrated ion but also some more complex ionic species (hydrolysis products).

3) The presence of such hydrolysis is indirectly supported by spectroscopic analysis – XPS.

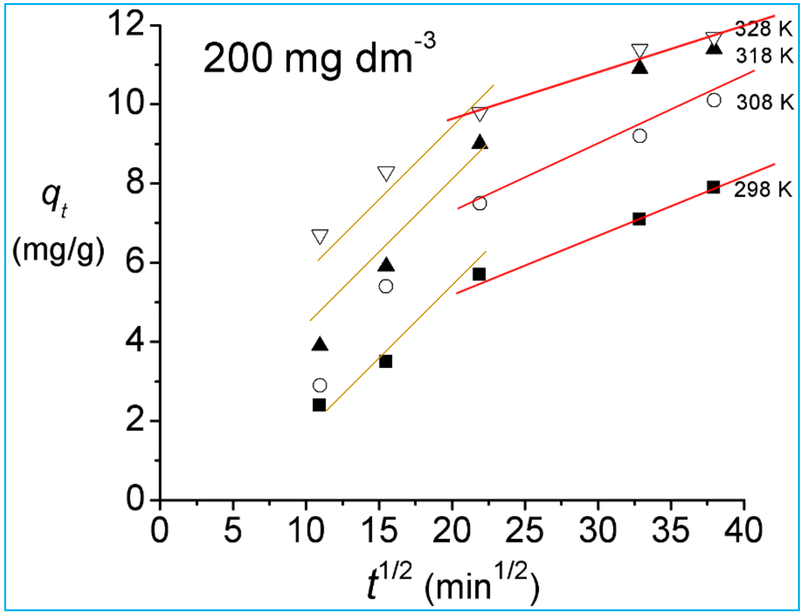
XPS gives Zn(II) concentration profile inside zeolite



XPS depth profiling as a function of the sputtering time

- Zn(II) concentration decreases slightly from the surface to the interior of the zeolite particles most probably due to the bulkiness of the Zn hydrolysis products.

Application of Weber-Morris model



$$q_t = k_d t^{1/2} + I$$

q_t (mg g^{-1}) - the adsorption capacity at time t (min),

k_d (mg g^{-1} min$^{-1/2}$) - the diffusion rate constant

I (mg g^{-1}) - the intercept at the ordinate.

The plots of q_t vs. $t_{1/2}$ give straight lines consisting of two segments:

1) The first segment due to film diffusion: the diffusion of the Zn ions through the boundary layer.

2) The second segment reflects a gradual adsorption stage, which is characterized by the intra-particle diffusion of Zn(II) into zeolitic vacancies.

C_0 (mg Zn dm^{-3})	T (K)	Weber–Morris model parameters*		
		k_{id} (mg g^{-1} min$^{-1/2}$)	I (mg g^{-1})	R^2
100	298	0.0932	2.05	0.999
	308	0.0590	4.26	0.999
	318	0.0590	5.36	0.999
	328	0.0827	5.01	0.991
200	298	0.136	2.71	0.997
	308	0.161	3.96	0.999
	318	0.153	5.69	0.986
	328	0.123	7.17	0.972
300	298	0.107	5.23	0.957
	308	0.165	5.42	0.991
	318	0.228	4.35	0.995
	328	0.0745	10.7	0.999
400	298	0.116	5.33	0.986
	308	0.140	7.37	0.991
	318	0.174	7.47	0.980
	328	0.0961	11.1	0.984

*The parameters refer to the second segment of the q_t vs $t^{1/2}$ line.

The second segment of the lines, describing the intraparticle diffusion, does not pass through the origin ($I > 0$).

This means that the intra-particle diffusion, although important over longer contact time periods, is not the rate-limiting step in the adsorption process.

Adsorption thermodynamics

Thermodynamic parameters can be calculated from the data obtained at different temperatures and the chosen initial $Zn(II)$ concentrations.

The standard free energy of adsorption ($\Delta G°$) is calculated as follows:

$$\Delta G° = -RT \ln K$$

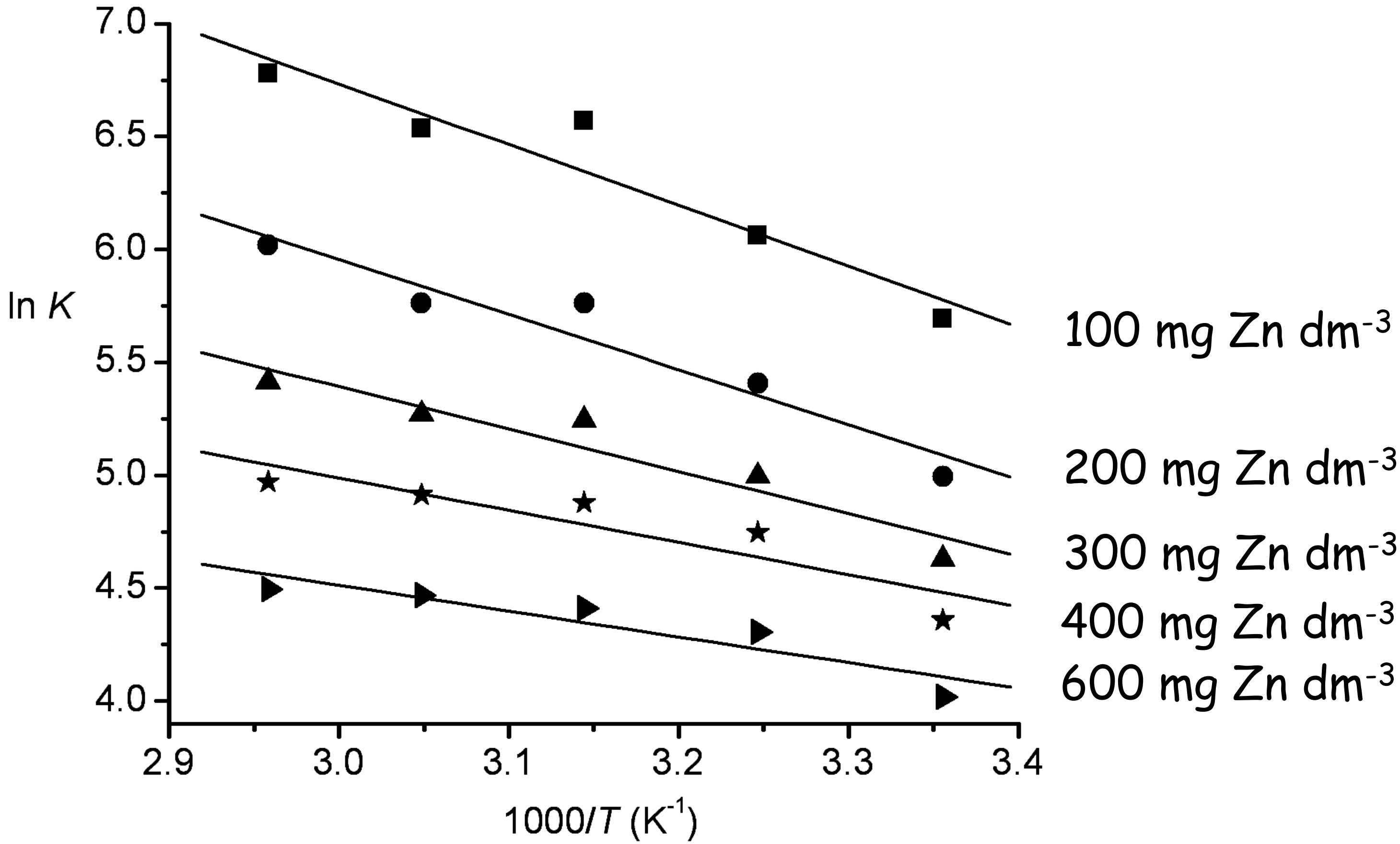
K is calculated as the ratio of the equilibrium concs of the $Zn(II)$ the zeolite and in solution (after 24 hours of contact).

- The enthalpy and entropy of adsorption can be calculated from the following equation:

- $$\ln K = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}$$

- the plot of $\ln K$ vs. $1/T$ gives a straight line (next slide); R - the universal gas constant

- $\Delta S°$ and $\Delta H°$ are evaluated from its intercept and slope, respectively.



The plots of ln K (K - the equilibrium constant) vs. 1/T for different initial Zn(II) concs.

C_0 (mg Zn dm^{-3})	T (K)	ΔG^o (kJ mol^{-1})	ΔH^o (kJ mol^{-1})	ΔS^o (J K^{-1} mol^{-1})	R^2
100	298	-14.1	22.4	123	0.915
	308	-15.5			
	318	-17.4			
	328	-17.8			
	338	-19.0			
200	298	-12.4	20.3	110	0.931
	308	-13.8			
	318	-15.2			
	328	-15.7			
	338	-16.9			
300	298	-11.5	15.6	91.6	0.913
	308	-12.8			
	318	-13.9			
	328	-14.4			
	338	-15.2			
400	298	-10.8	11.8	77.0	0.826
	308	-12.1			
	318	-12.9			
	328	-13.4			
	338	-14.0			
600	298	-10.0	9.49	66.0	0.855
	308	-11.0			
	318	-11.7			
	328	-12.2			
	338	-12.6			

What can be concluded?

- The adsorption is spontaneous ($\Delta G°$ < 0). The spontaneity slightly increases with temperature for all initial Zn(II) concs.

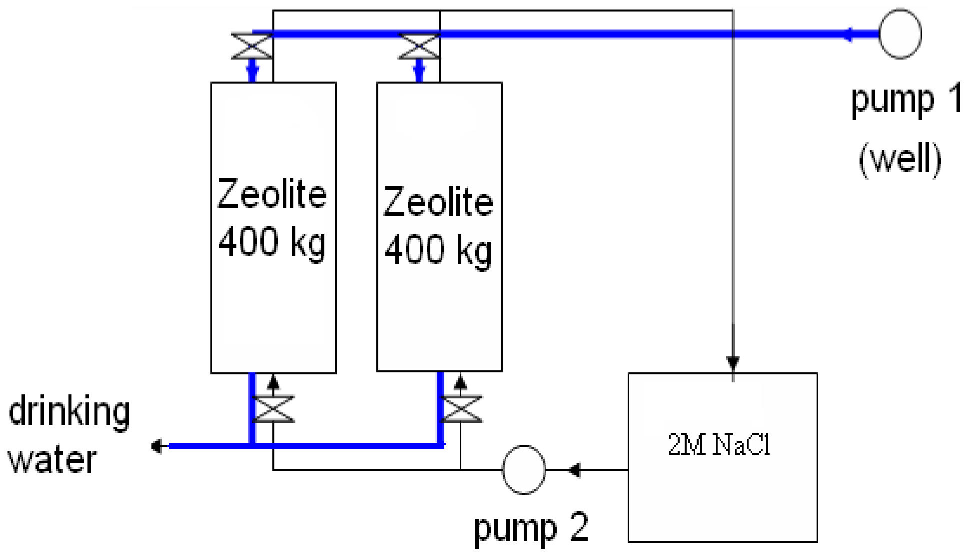
- The adsorption is endothermic ($\Delta H°$ >0).

- $\Delta S°$ is positive (the adsorption involves the liberation of two Na^+ ions when one Zn^{2+} ion is bound to the adsorbent).

- The spontaneity (at a given temperature), as well as the $\Delta H°$ and $\Delta S°$ values all decrease as the initial Zn(II) concentration increases.

Pilot plant for improval of drinking water quality

12,096 m^3/day (~ 120 inhabitants)



A pilot installed in 2013 in a small village in Serbia. The plant significantly decreased operational by replacing synthetic polymer resins.

Removal of Mg^{2+} and recovering of the saturated zeolite proceed intermittently.

S. Tomic et al, Clay Mineral, 47 (2012) 81-92

Zeolites in catalysis

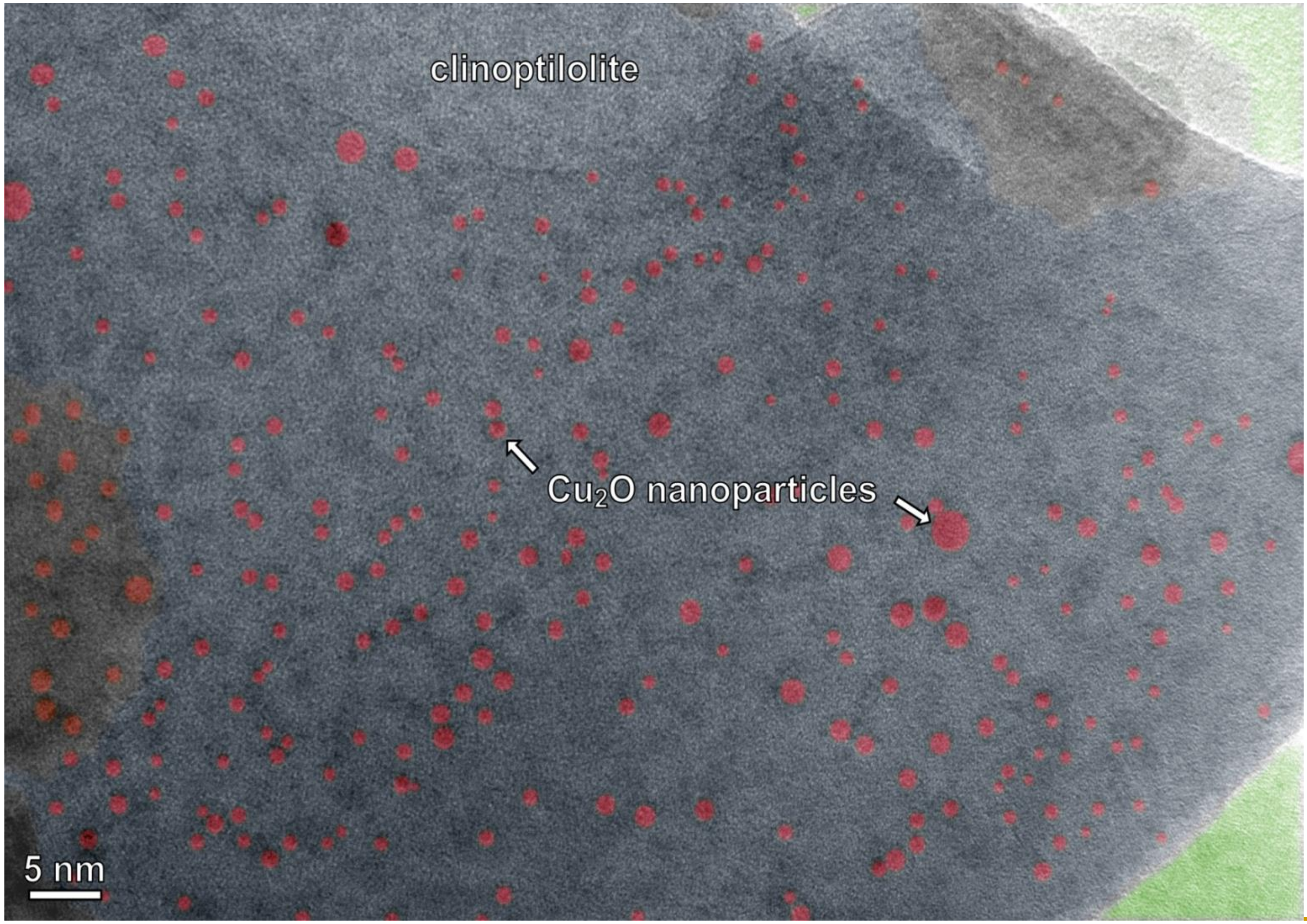
- Suitable support of ultra fine nano-sized oxide particles (up to 10 nm); catalytic activity proved in lignin pyrolysis, esterification of levulinic acid.

- Suitable support of oxides with photolytic activity under Solar irradiation.

Refs:

N. Rajic et al., Micropor Mesopor Mater 176 (2013) 162-167
J. Pavlovic et al, Micropor Mesopor Mater 279 (2019) 10-18
A. Suligoj et al., Catalysts 19 (2020) 253

Formation of nano-oxide particles inside zeolitic lattice



N. Rajic et al., J Phys Chem Solids 72 (2011) 800-803

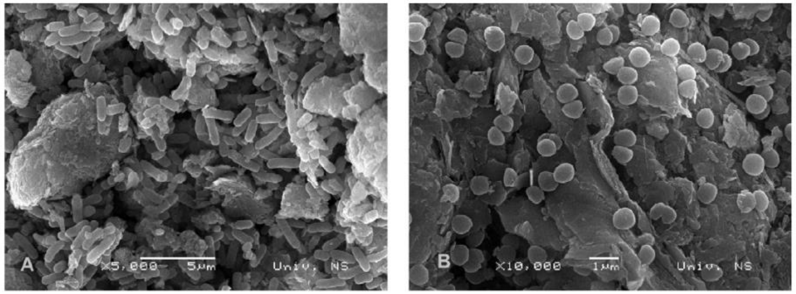
Antimicrobial activity

•Gram- positive:
✓*Staphylococcus aureus*, DSM 799)

•Gram-negative:
✓*Escherichia coli* (DSM 498)
isolates of *E. coli* from the waterborne in Serbia
✓*Acinetobacter baumannii* (EU clone I and II)

Antimicrobial activity

Antibacterial activity against coliforms (*E. coli* and *S. aureus*)



Bacteria	Medium	Cu-Cli		Zn-Cli		Ag-Cli
		Reduction (%) for different time (h)				
		1	24	1	24	1-24 h
E. coli DSM 498	Real effluent	40.1	93.5	8.09	95.1	100
	Synthetic water	19.4	94.9	6.27	93.9	100
S. aureus DSM 799	Real effluent	55.7	86.8	2.79	82.1	100
	Synthetic water	42.8	87.3	3.31	82.3	100

J. Hrenović, et al., J. Hazard Mat 201 (2012) 260-264.