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School of Mineral Resources Engineering

Adsorption of copper from aqueous solutions on synthetic zeolites produced from Greek fly ash: Kinetic and equilibrium studies

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Outline

1. Introduction
2. Experimental process
   - synthesis
   - batch adsorption experiments
3. Results
   - Zeolite characterization (XRD, FTIR)
   - Adsorption capacity of synthetic zeolites for Cu(II) ions:
   - Kinetics (1^{st}, 2^{nd} order)
   - Isotherms (Langmuir, Freundlich)
4. Conclusions

Introduction I. Fly ash

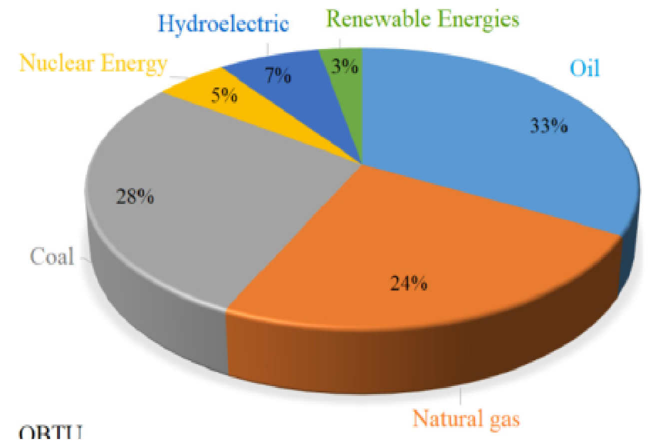
Coal is the **second** major fossil fuel source for energy production among other energy sources

Fly ash (FA) used in this study: by-product of the thermoelectric power station in Megalopolis (Peloponnese, Greece) produced from coal combustion

→ annual production: 12·10^{6} tons

→ only 10% of the produced fly ash is used in the cement industry as pozzolanic additive to improve properties of concrete

→ 90% of fly ash is disposed of in abandoned mining sites and causes environmental problems

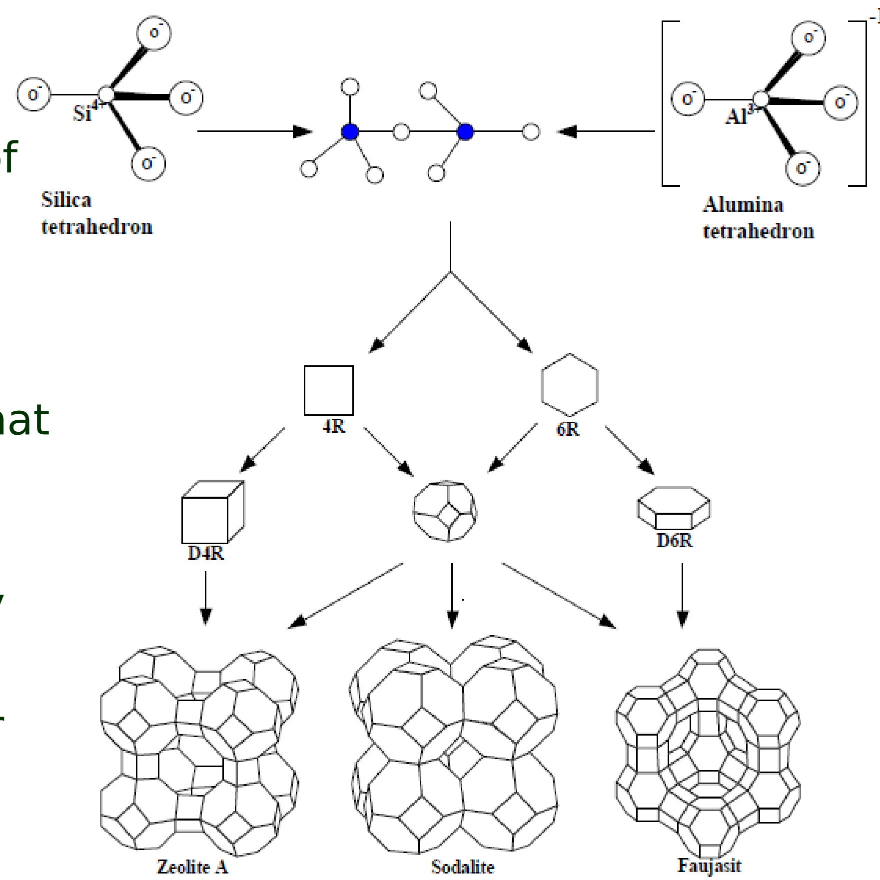


(Hosseini Asl et al., *J. Cleaner Prod.* **2019**, *208*, 1131)

Introduction II. Zeolites

Zeolites: crystalline, microporous aluminosilicates
with a basic crystalline framework composed of **SiO_4**
and **AlO_4** tetrahedra connected with shared oxygen
atoms, and forming characteristic structures that result in excellent performance in multiple applications :
 as candidate **adsorbent materials** are very attractive
due to cost-effectiveness & good selectivity for heavy metals
3 types of zeolites: natural, modified, & **synthetic**
 Fly ash contains significant amounts of crystalline and amorphous aluminosilicates, can be used for **zeolite production**

Converting fly ash into zeolites not only partially solves the disposal problem but also converts a potentially hazardous material into a value-added, marketable product



Structural units of zeolite-A, sodalite & faujasite
(Masoudian et al., *Bull. Chem. React. Eng. Catal.* **2013**, *8*, 54)

State-of-the-art

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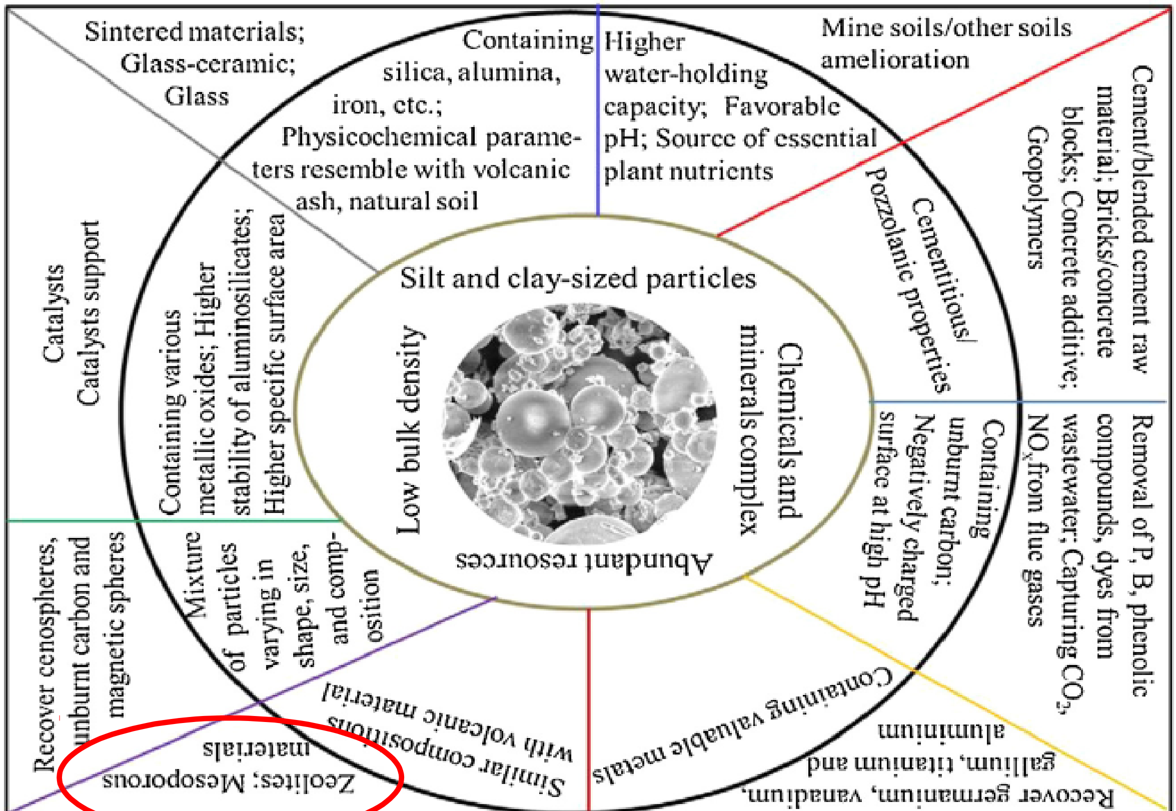


Fig. 1. Various applications of coal fly ash [14] (After Simate et al., *J. Environ. Chem. Eng.* ***2016,*** *4,* 229

Several studies investigated the **conversion of fly ash to zeolites** and their adsorption efficiency for heavy metals, organics & gaseous pollutants

Aim of this study..

- **Production of zeolites from Greek lignite fly ash from Megalopolis by alkaline fusion**
- **Characterization of synthetic zeolites**
- **Kinetics models**
- **Adsorption equilibrium**
- **Regeneration experiments**

Experimental process: Synthesis of zeolites

XRF analysis of FA

Major components % w/ w	Fly ash Megalopolis (FA)
SiO_2	**43.13**
CaO	18.74
Al_2O_3	**13.07**
$Fe_2O_{3(tot)}$	12.40
MgO	2.65
MnO	0.1
Na_2O	1.40
K_2O	2.33
P_2O_5	0.21
TiO_2	1.11
SO_3	4.56
Cr_2O_3	0.06
LOI	4.67
Total	104.43
Si/ Al	**2.91**

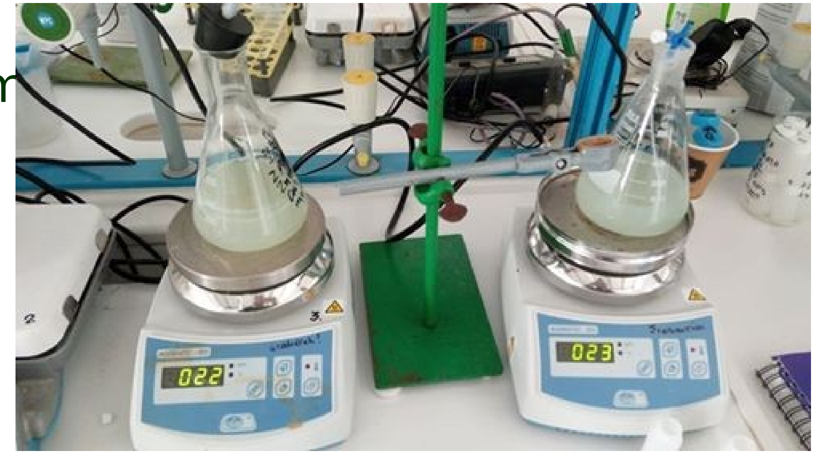
Synthetic Zeolites:
- alkaline fusion (with NaOH) of FA at 600 °C for 1 h
- mass ratios of FA to NaOH: 1:1 (**ZFA1**) and 1:1.5 (**ZFA1.5**)
- pulverized and mixed with H_2O (in a constant ratio of 20% w/v) under overnight stirring
- after incubation of the suspension at **low** temperature

(30 °C for 4 days) the synthesized zeolites were obtained after centrifugation and drying at 80 °C for 24 h

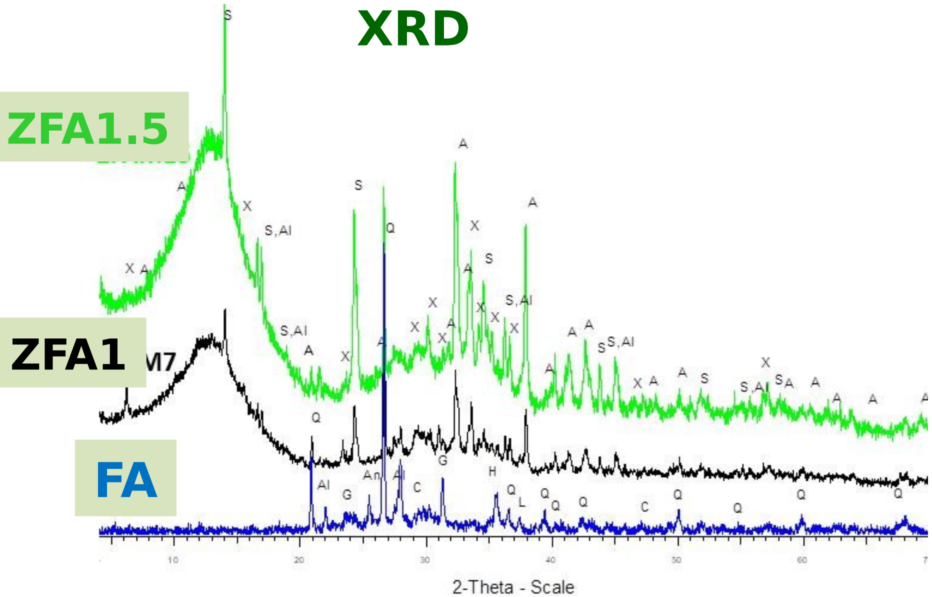
Experimental process: Batch experiments

xperimental conditions:

- $Cu(NO_3)_2$ solution concentration: 50-200 m
- Adsorbent (zeolite) dosage: 0.3-1.5 g.L^{-1}
- constant ionic strength NaCl 0.1 M
- working volume: 250 mL
- stirring at 600 rpm
- room temperature
- filtration (0.45μm PTFE) Cu(II) by AAS

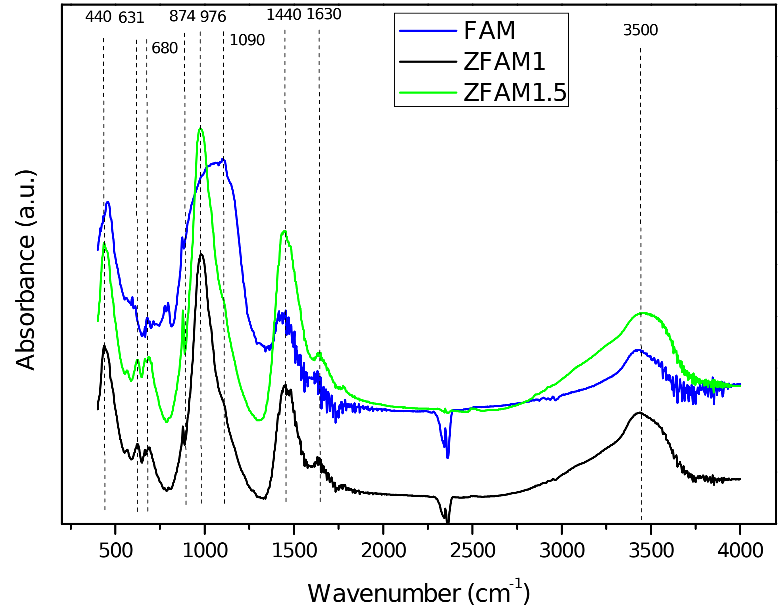


Results I. Characterization of synthetic zeolites



Q: Quartz, SiO_2
Al: Albite, $NaAlSi_3O_8$
G: Gehlenite, $Ca_2Al_2SiO_7$
An: Anhydrite, $CaSO_4$
H: Hematite, Fe_2O_3
L: Lime, CaO
C: Calcite, $CaCO_3$
X: Zeolite X, $NaAlSi_{1.23}O_{4.46}\cdot 3.07H_2O$
A: Zeolite A, $NaAlSi_{1.1}O_{4.2}\cdot 2.25H_2O$
S,Al: Sodium aluminium silicate hydrate, $Na_6Al_6Si_{10}O_{32}\cdot 12H_2O$

FTIR



3500cm^{-1}: stretching vibration (-OH, HOH)
1630cm^{-1}: bending vibrations (HOH)
1440cm^{-1}: stretching vibrations (O-C-O)
1090, **976cm^{-1}**: asymmetric stretching vibration
874, 680, 631cm^{-1}: symmetric stretching vibrations (Si-O-Si, Al-O-Si)
440cm^{-1}: bending vibration (Si-O-Si and O-Si-O)

Results II. Kinetic studies

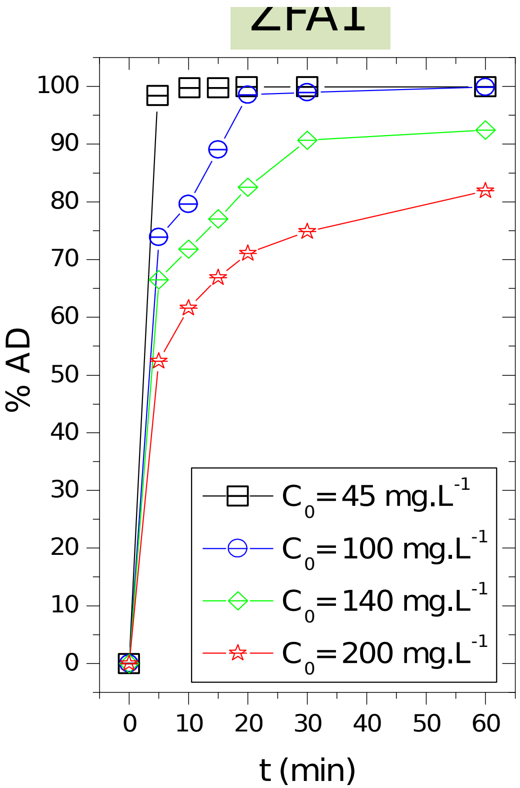
ffect of initial Cu(II) concentration

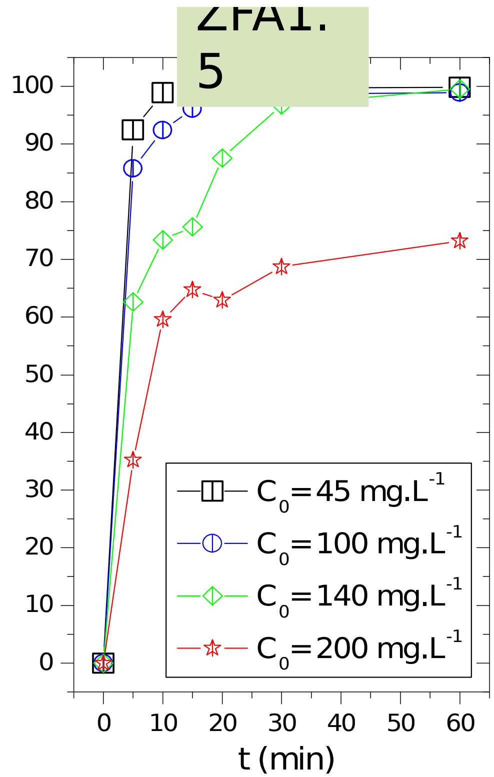
Effect of initial Cu(II) concentration on the adsorption capacity of **ZFA1** and **ZFA1.5** (dosage 0.5 g·L^{-1},
pH 4.4)

$$\%AD = \frac{(C_0 - C_t)}{C_0}\%$$

C_0, C_t: initial and measured Cu(II) concentrations in solution during adsorption

C_0, C_t: initial and measured Cu(II) concentrations **in solution** during adsorption





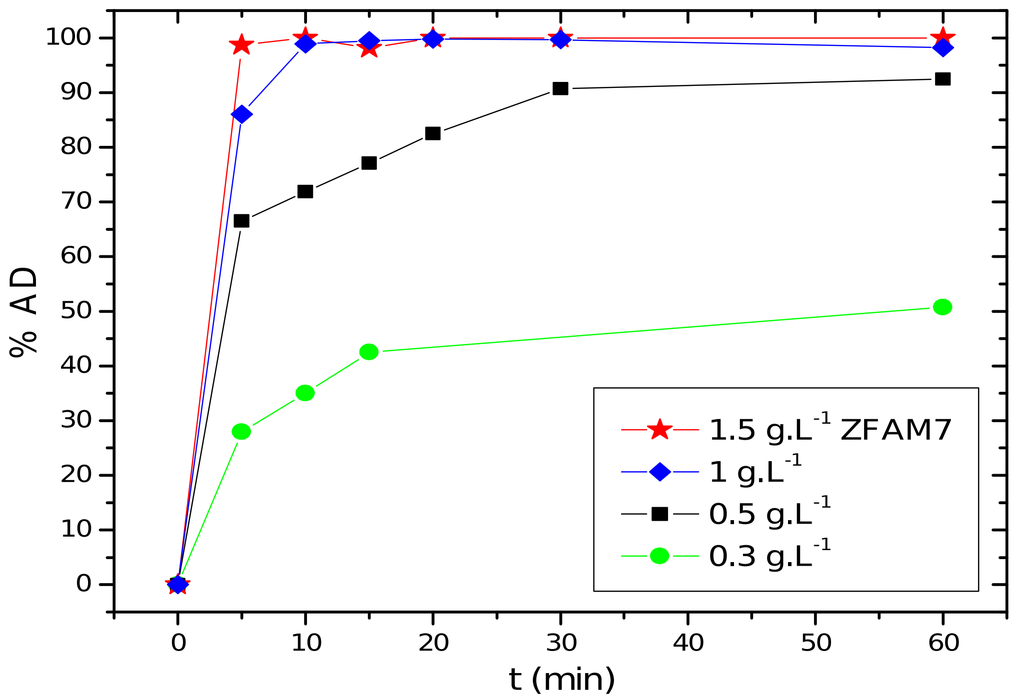
- The adsorption capacity decreases when the initial Cu(II) concentration increases until the system reaches equilibrium
- At Cu(II) 200mg.L^{-1} **%AD (ZFA1)** was greater to **%AD (ZFA1.5)**

Results II. Kinetic studies

ffect of the adsorbent dosage

Effect of adsorbent dosage ($g \cdot L^{-1}$) on the adsorption efficiency of **ZFA1** (initial Cu(II) concentration of
140 $mg \cdot L^{-1}$; pH 4.4)

ZFA1

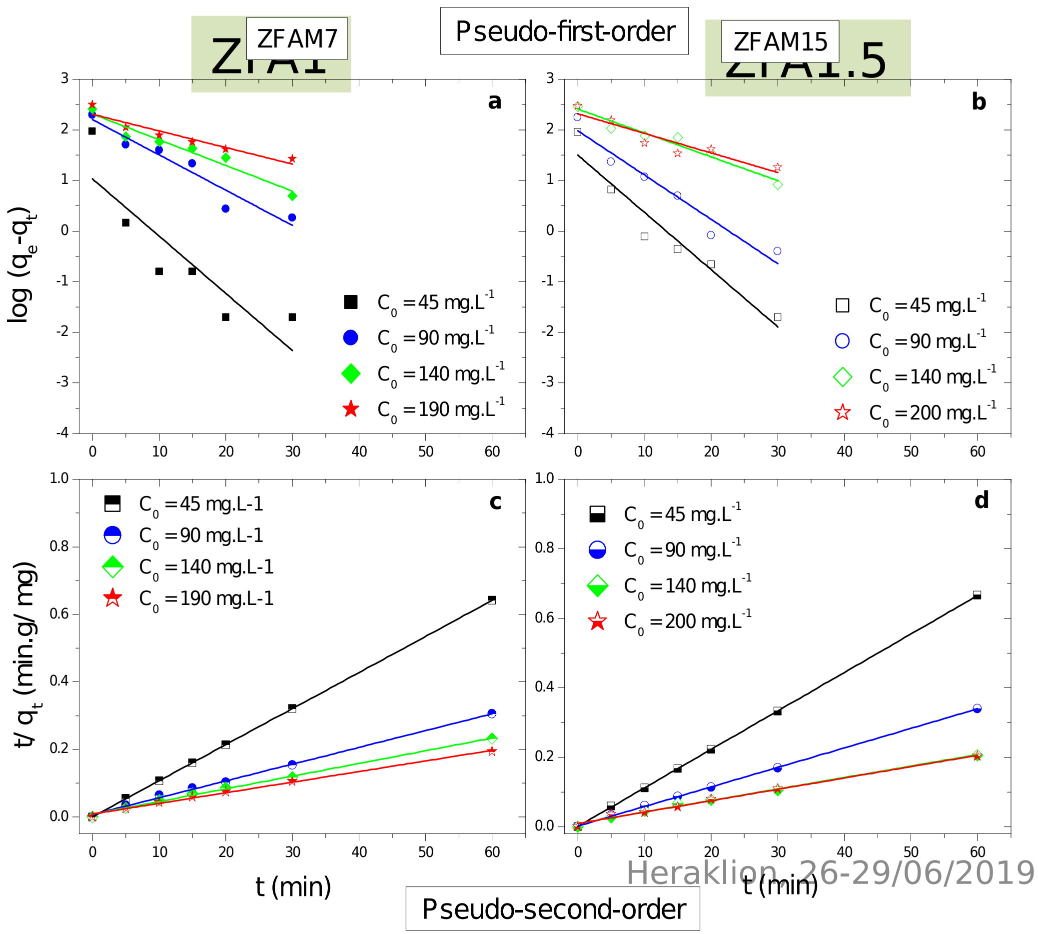


- Increase of adsorbent dosage resulted in increase of Cu(II) adsorption due to the increase of the number of available adsorption sites
- At low dosage (0.3 $g \cdot L^{-1}$) the adsorption degree of **ZFA1** decreased by 55% compared to the adsorption capacity at higher dosage (1.5 $g \cdot L^{-1}$)
- Kinetic modelling at dosage of 0.5 $g \cdot L^{-1}$

Results II. Kinetic modelling

Pseudo-first & pseudo-second-order adsorption of Cu(II) onto 0.5 $g.L^{-1}$ **ZFA1** (a, c) and **ZFA1.5** (b, d) synthesized zeolites

$log(q_e - q_t) = log\, q_e - \frac{k_1 t}{2.303}$	Eq. 6 1st order	**1st order**
$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$	Eq. 7 2nd-order	
$log(q_e - q_t) = log\, q_e - \frac{k_1 t}{2.303}$	Eq. 6 1st order	**2nd-order**
$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$	Eq. 7 2nd-order	

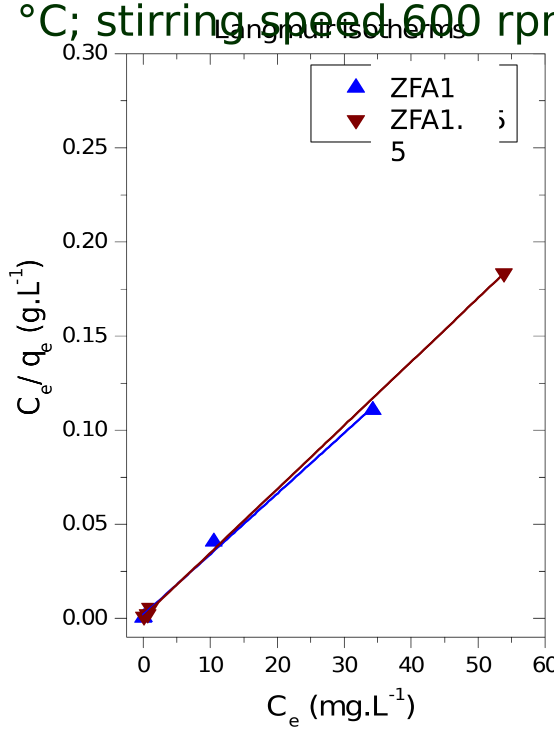


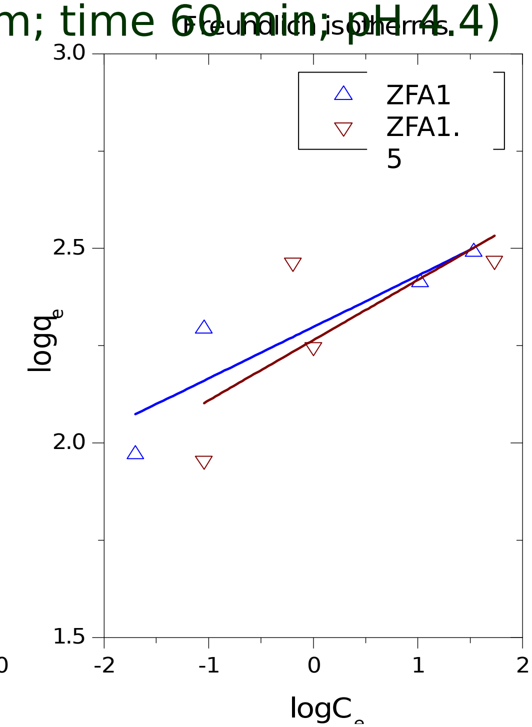
- The experimental data fit well the **pseudo-second order** kinetic model
- The rate constant k_2, however, depended on the initial concentration of Cu(II) ions in solution, indicating that **surface diffusion** instead of chemisorption of Cu(II) ions at the adsorption sites of synthetic zeolites is the **rate determining step**

Results III. Equilibrium isotherms

Experimental and modelled Cu(II) adsorption isotherms for synthetic zeolites, **ZFA1** and **ZFA1.5** using Langmuir and Freundlich equations (Cu(II) concentration of 50 to 200 mg.L-[1], dosage 0.5 g.L-[1]; θ 25 °C; stirring speed 600 rpm; time 60 min; pH 4.4)

$q_t = \frac{V(C_o - C_t)}{m}$		
$\frac{C_e}{q_e} = \frac{1}{k_l q_m} + \frac{C_e}{q_m}$	Langmuir	
$\log q_e = \log k_f + \frac{1}{n} \log C_e$	Freundlich	
$q_t = \frac{V(C_o - C_t)}{m}$		**Langmuir**
$\frac{C_e}{q_e} = \frac{1}{k_l q_m} + \frac{C_e}{q_m}$	Langmuir	
$\log q_e = \log k_f + \frac{1}{n} \log C_e$	Freundlich	
$q_t = \frac{V(C_o - C_t)}{m}$		**Freundlich**
$\frac{C_e}{q_e} = \frac{1}{k_l q_m} + \frac{C_e}{q_m}$	Langmuir	
$\log q_e = \log k_f + \frac{1}{n} \log C_e$	Freundlich	





	Langmuir isotherm				Freundlich isotherm		
	q_m	k_l	R^2	R_L	k_f	n	R^2
	mg·g^{-1}	L·mg^{-1}				g·L^{-1}	
ZFA1	310.6	1.7	0.994	0.0052	198.7	7.5	0.825
ZFA1.5	295.9	3.4	0.999	0.0049	152.2	5.6	0.904

- the adsorption data is best fitted by the **Langmuir** equation. Langmuir model suggests a monolayer adsorption of Cu(II) on the outer surface of zeolites (**ZFA1** and **ZFA1.5**).
- The highest equilibrium adsorption capacity obtained for Cu(II) was **311** and

Results IV. Regeneration

Regeneration degree (%RD) of **ZFA1.5.** Experimental conditions: 0.05 M Na_2EDTA and 0.1 M NaCl; dosage 5 $g \cdot L^{-1}$; θ 25 °C; 600 rpm; pH 4.4.

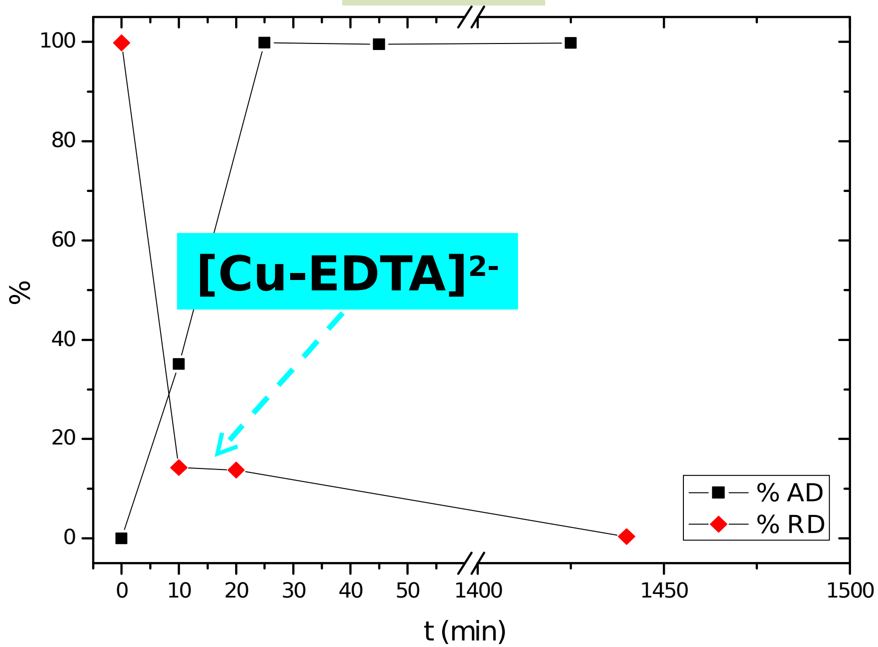
$\%AD = \frac{(C_0 - C_t)}{C_0}\%$	C_0, C_t: initial and measured Cu(II) concentrations **in solution** during adsorption
$\%RD = \frac{(m_0 - m_t)}{m_0}\%$	m_0, m_t: initial and measured amount of Cu(II) adsorbed **into zeolite**

$\%AD = \frac{(C_0 - C_t)}{C_0}\%$	C_0, C_t: initial and measured Cu(II) concentrations **in solution** during adsorption
$\%RD = \frac{(m_0 - m_t)}{m_0}\%$	m_0, m_t: initial and measured amount of Cu(II) adsorbed **into zeolite**

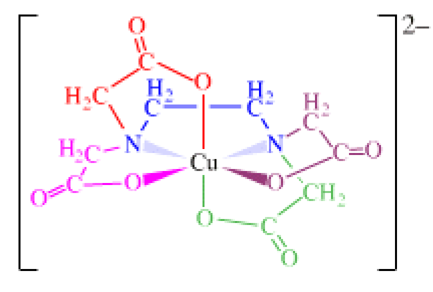
C_0, C_t: initial and measured Cu(II) concentrations **in solution** during adsorption

m_0, m_t: initial and measured amount of Cu(II) adsorbed **into zeolite**

ZFA1.5



- **Regeneration** degree of **ZFA1.5** was 20% in 10 min and Cu(II)-adsorbed-ZFA1.5 was completely removed by Na_2-EDTA solution fo
  Cu(II)-EDTA comple
  $[Cu\text{-}EDTA]^{2-}$ (>20 m



Followed by adsorption *degree of Cu(II) onto* ***ZFA1.5*** *increased rapidly to 35% in 10 min and became constant, 100% indicating that the removal of Cu(II) mainly occurred within 30 min*

- **ZFA1.5** was successfully regenerated by Na_2EDTA solution

Conclusions

- **Greek fly ash** has been converted to **zeolite** through alkaline fusion at 600 °C for 1 h using mass ratio of **FA to NaOH 1:1 and 1:1.5**. After fusion incubation of the obtained suspended solids in distilled water was carried out at **low temperature (**30 °C) for 4 days
- Mineralogical analysis of zeolites revealed the presence of zeolite A, zeolite X and sodalite
- Both **ZFA1** and **ZFA1.5** zeolites exhibited high Cu(II) ions removal efficiency (100%). The experimental data fit well the **pseudo-second order kinetic model**
- Adsorption data (adsorbents **ZFA1** and **ZFA1.5**) are best fitted by the **Langmuir** equation suggesting a monolayer adsorption of Cu(II) on the outer surface of zeolites
- Highest equilibrium adsorption capacity obtained for **Cu(II)** was **311 and 296 mg·g^{-1} for ZFA1 and ZFA1.5**, respectively
- **ZFA1.5** was successfully **regenerated** by Na_2EDTA solution 0.05 M

Acknowledgments..

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https://www.invalor.org/

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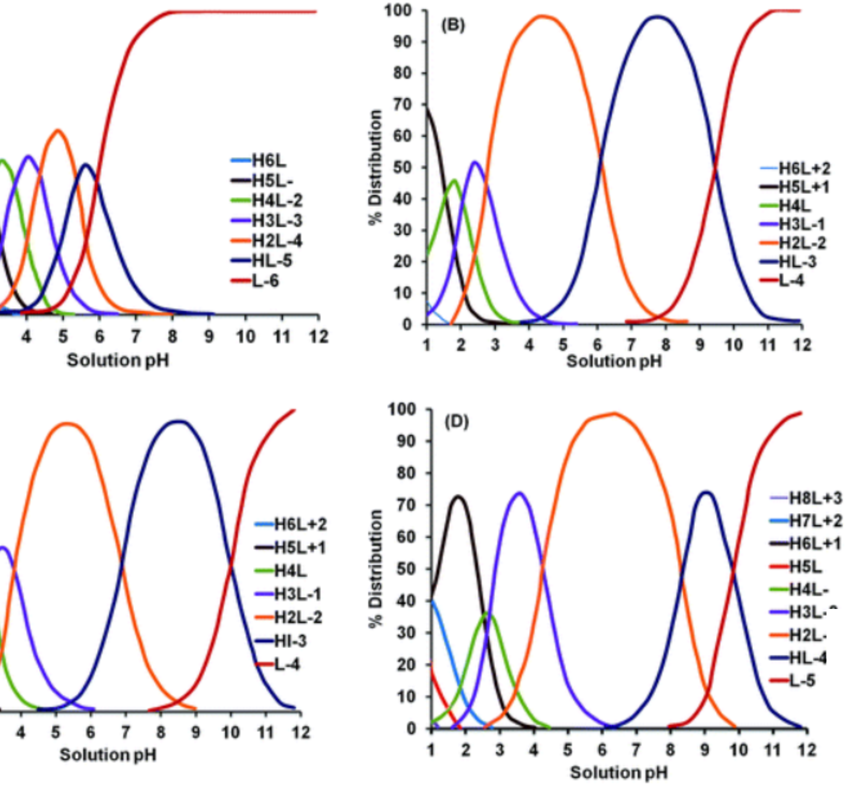
Thank you for your attention..



protonation stages of various chelating agents: (A) TDS, (B) EDTA, (C) EDD

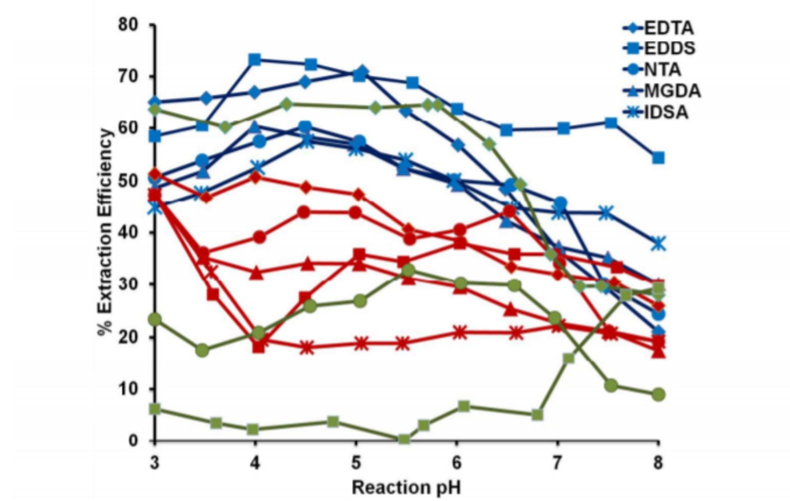


Figure 6: Effect of reaction pH on extraction efficiency of various chelating agents for Cu (Blue markers), Zn (Red markers) and Pb (Green markers)104
294x207mm (300 x 300 DPI)