Zn^{2+} and Cd^{2+} removal from wastewater using clinoptilolite as adsorbent

C. GALLETTI, M. DOSA, N. RUSSO, D. FINO

CREST
Catalytic Reaction Engineering for Sustainable Technologies

Applied Science and Technology Department
Politecnico di Torino
*Torino, **Italy***

HEAVY METALS REMOVAL METHODS

- The conventional method for the removal of heavy metal from industrial wastewater generally involves a **chemical precipitation process.**
- Studies on the treatment of effluents containing heavy metals have shown that **adsorption** is a highly effective technique for the removal and **activated carbon** is extensively used.

BUT…

- the use of activated carbon is not suitable in developing countries due to the **high costs** associated with production and **regeneration** of spent carbon,
- the possibility to remove heavy metals by means of adsorption using different and **low cost** adsorbents has been evaluated.

→ natural zeolites *ion-exchange* + *properties* *molecular sieve*

METAL LAW LIMITS

Zinc:

WHO Guidelines for drinking-water quality 2006

 Zn^{2+} concentration **below 5 mg/L**

Italian Legislative Decree 1999

→ Zn^{2+} concentration **below 0.5 mg/L** for waste in surface water

→ Zn^{2+} concentration **below 1 mg/L** for wastewater released in public drainage system.

Cadmium:

WHO Guidelines for drinking-water quality 2011

→ Cd^{2+} concentration **limited to 0,003 mg/L**

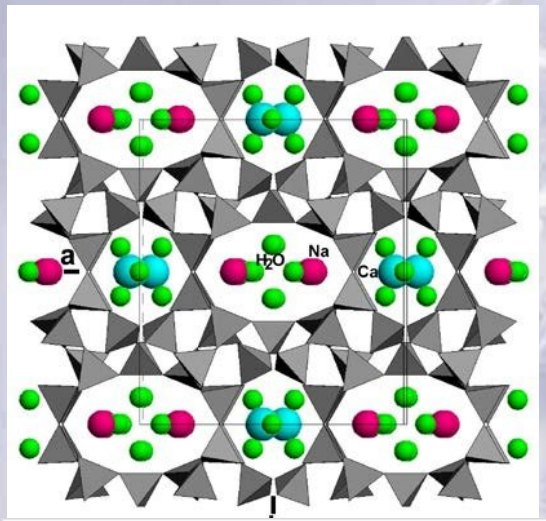
Italian national legislation (D. Lgs. 2006/152)

 limits Cd^{2+} concentration **less then 0.02 mg/L** for superficial water and wastewater;

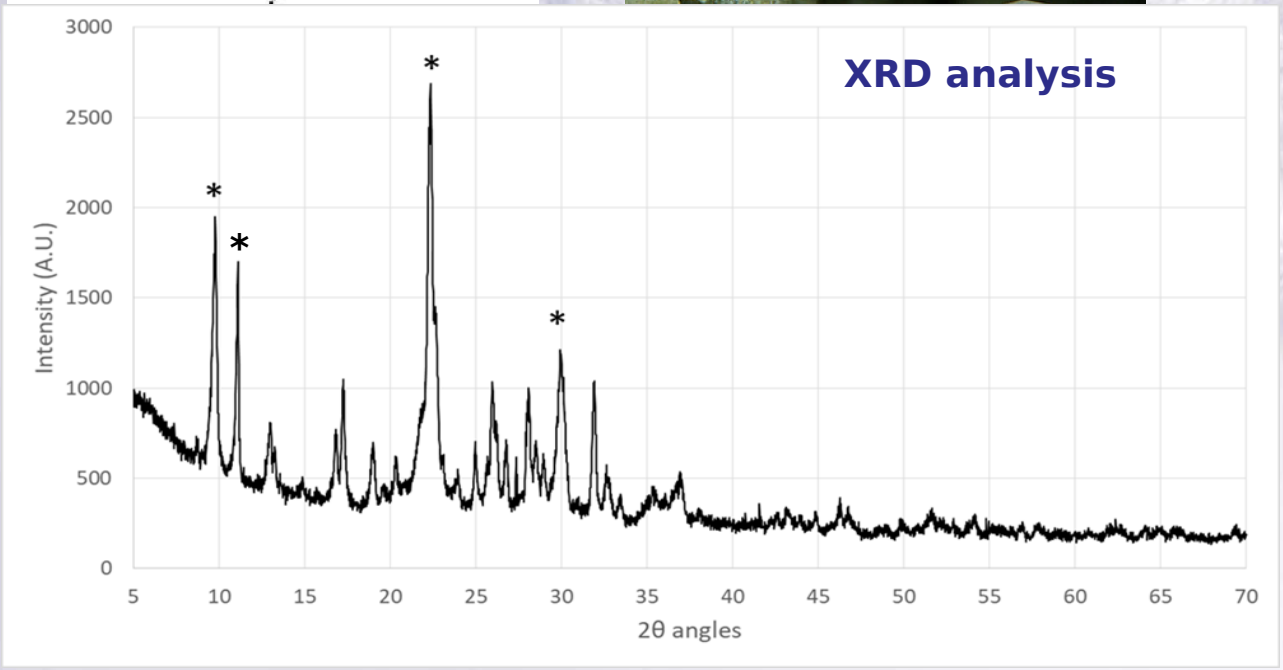
→ Cd^{2+} concentration **below 0.03 mg/l** in domestic wastewater.

ADSORBENT

Clinoptilolite: $(Na,K,Ca)_2\text{-}3Al_3(Al,Si)_2Si_{13}O_{36}\cdot 12H_2O$



Clinoptilolite is a hydrated alkali aluminosilicate and it is one of the most abundant zeolite. Its structure consists of a framework of silica and alumina tetrahedra, within which water molecules and exchangeable cations (e.g., calcium, potassium, sodium) migrate.



- high crystallinity of the clinoptilolite sample
- at 2θ = 22.3° there was the most intense peak of the clinoptilolite
- other intense peaks, characteristic of the clinoptilolite material, were identified at 2θ = 9.8°, 11° and 29.9°.

METHODOLOGY OF ADSORPTION TEST

clinoptilolite

Liquid samples at different time

$Cd(NO_3)_2 \cdot 4H_2O$
$ZnSO_4 \cdot 7H2O$

ICP-MS

Cd^{2+} and Zn_2^+ concentratrion (C)

Adsorption capacity

$$\frac{C_0 - C}{C_0} \times 100$$

Operating conditions:

- Metal concentration = 10,50,100,200 mg/L
- Adsorbent concentration = 10,15,20,40,60 g/L
- Optimized pH_0 = 4.5

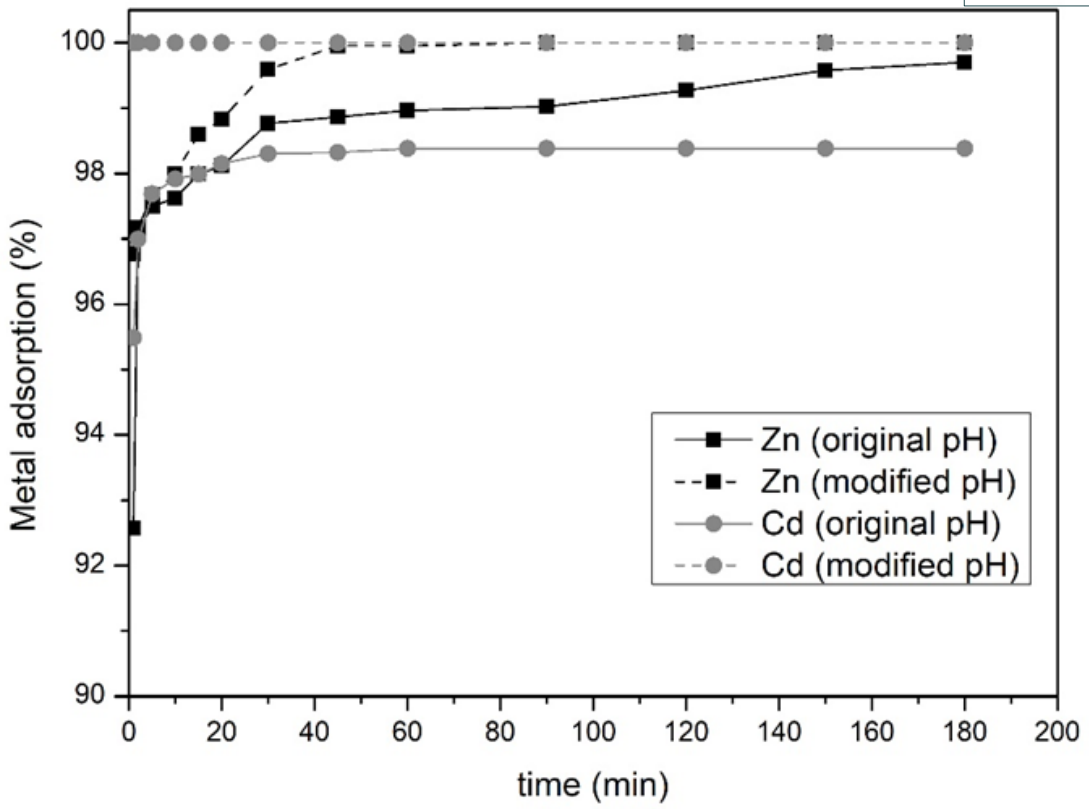
OPTIMIZATION OF pH CONDITIONS

At **lower pH** values H^+ ions competed with metal ions for sites on the surface of the adsorbent, thereby hindering Zn and Cd ions from reaching such sites through the action of repulsive forces. At **higher pH** values, the metal ions could precipitate as hydroxide and did not get adsorbed.

Operating conditions:

- Metal concentration = 10 mg/L
- Adsorbent concentration = 10 g/L

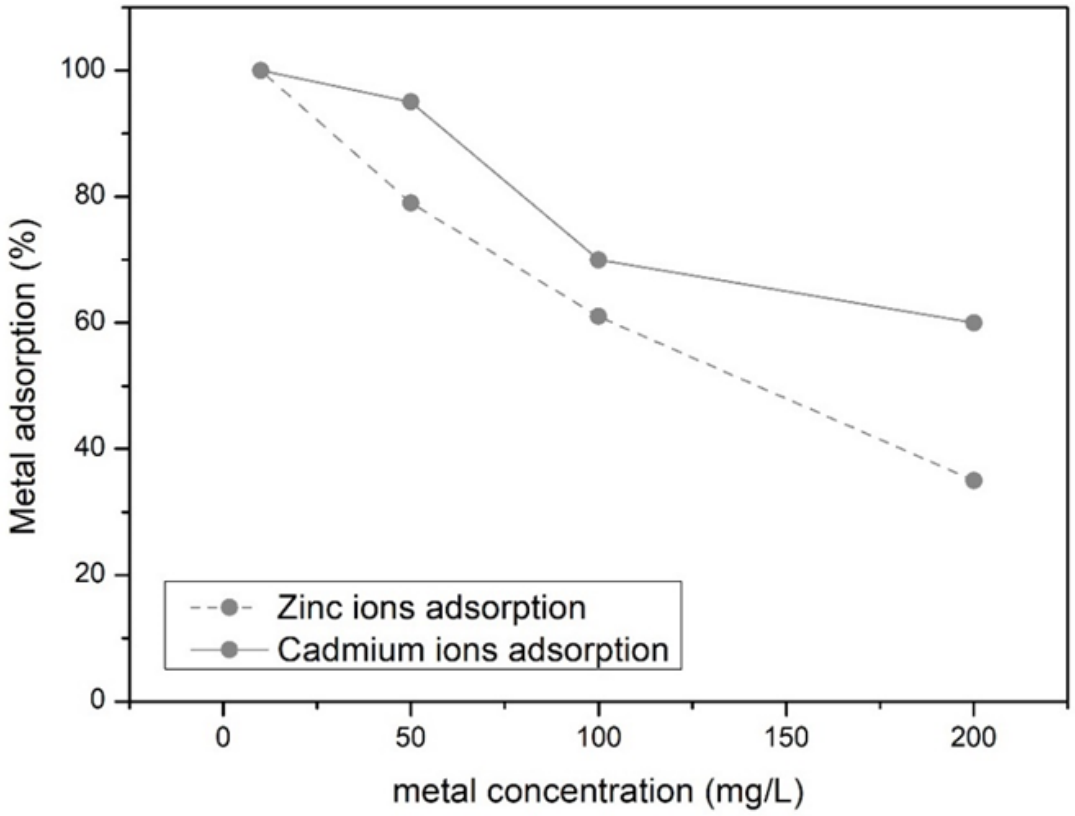
pH_0 = 3,6
modified pH_0 = 4,5



pH_0 = 4,5

ADSORPTION TEST IN SINGLE SYSTEM

10 g/L clinoptilolite



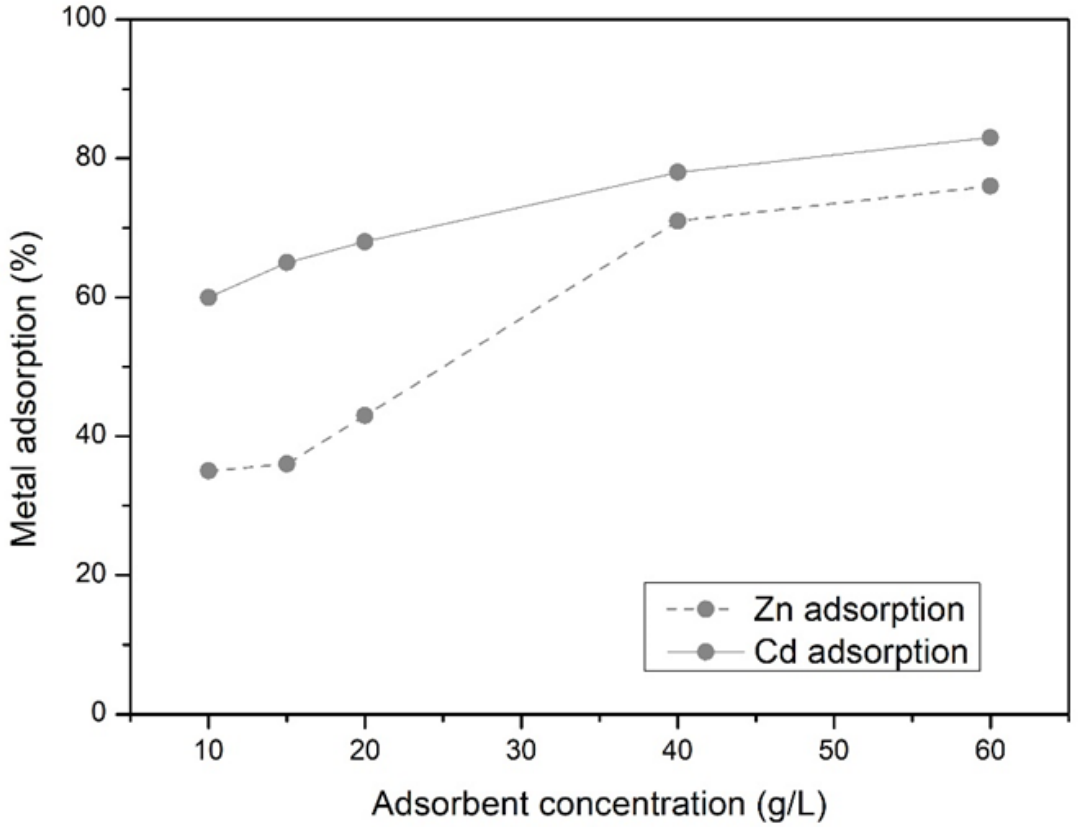
- For both zinc and cadmium ions, complete adsorption was reached with metal concentration equal to 10 mg/L.
- Increasing metal amount progressively to 50, 100 and 200 mg/L, maximum adsorption capacity decreased.
- Maximum adsorption capacity for Zn^{2+} decreases down to 35% with 200 mg/L of metal in the starting solution.
- Cadmium ions removal always remained above 50% even at high metal concen ions.

For next tests:

- metal concentrations = 200 mg/L
- different clinoptilolite

ADSORPTION TEST IN SINGLE SYSTEM

200 mg/L metal

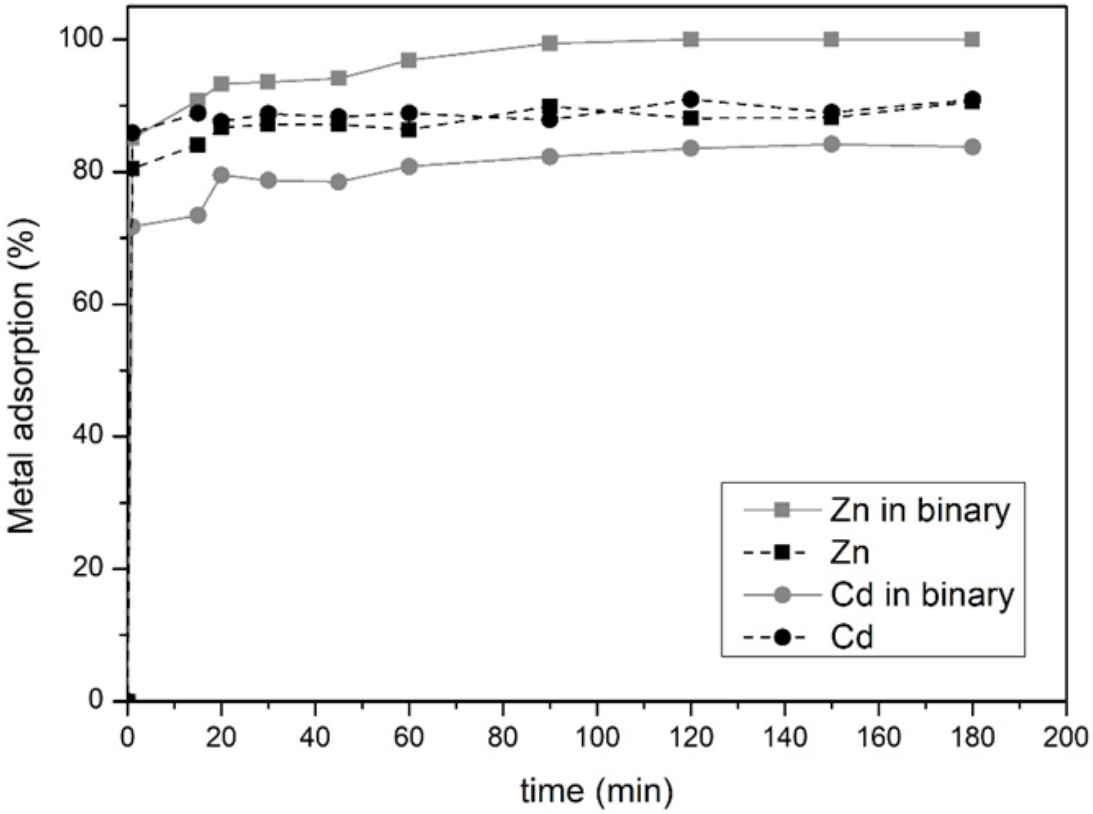


- Maximum adsorption percentages increased for the both zinc and cadmium.
- According to previous results, zeolite shown higher abatement capacity towards Cd^{2+}.
- By increasing clinoptilolite concentration to 40 g/L, ions abatement exceeded 50%, for both the metals.
- Adsorption capacity did not vary much more enhanced concentration to 60 g/L.

- ✓ Adsorption of zinc and cadmium ions onto clinoptilolite had a ion-exchange nature and the obtained results confirmed higher natural zeolite affinity for cadmium ions.
- ✓ The molecular sieve property of zeolite influenced adsorption as Cd^{2+} had a hydrated ionic radius lower than Zn^{2+} (3,8 Å vs. 4,4 Å) that permitted entering the pores of clinoptilolite (about 4 Å).

ADSORPTION TEST IN BINARY SYSTEM

- 40 g/L clinoptilolite
- 100 mg/L Zn^{2+} + 100 mg/L Cd^{2+}



- When the two metals were present in solution individually, they were adsorbed over time with a very similar trend.
- In the binary system there was a greater affinity of zinc with clinoptilolite.

- In binary system some competitive mechanisms take place and have to be investigated.
- Ion behaviors confirmed a literature study (Sellaoui, 2017) on adsorption energies showing that the zinc adsorption capacity was not influenced by cadmium presence while cadmium adsorption was reduced by zinc presence in binary system.

CHARACTERIZATION AFTER ADSORPTION

XRF analysis

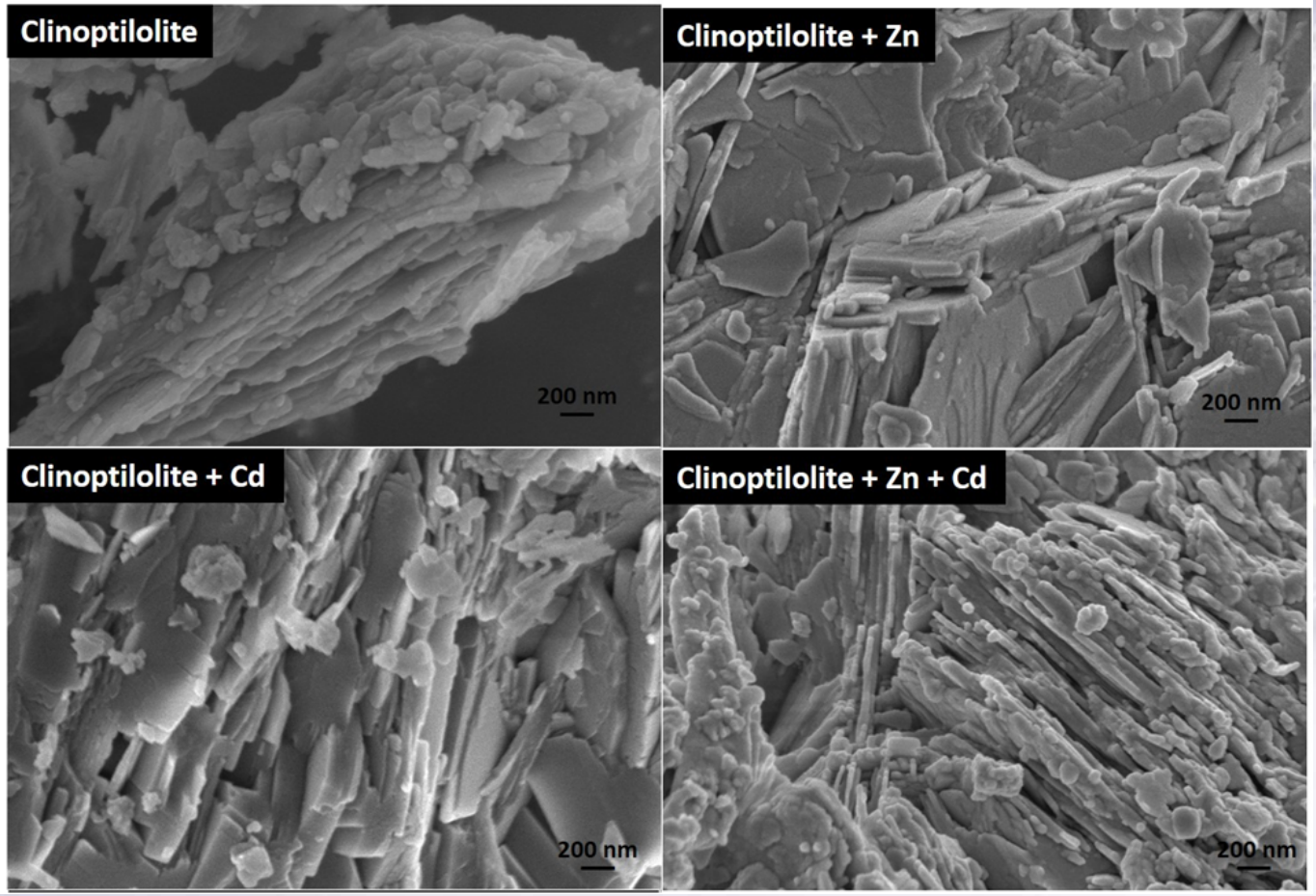
on fresh and used clinoptilolite

	Al_2O_3	SiO_2	K_2O	CaO	ZnO	CdO
	%mass	%mass	%mass	%mass	%mass	%mass
clinoptilolite	12,6	76,6	4,77	3,92	-	-
clinoptilolite+Zn	12	77,2	4,82	3,78	0,876	-
clinoptilolite+Cd	13,5	74,6	4,85	3,42	-	0,619
Clinoptilolite+Zn +Cd	12,6	76,7	5,02	4,09	0,337	0,201

- The main elements of clinoptilolite were silica and alumina.
- Potassium and calcium were present in minimum quantities.
- Cadmium and zinc were not present in the fresh zeolite, but only after adsorption processes.

CHARACTERIZATION AFTER ADSORPTION

FESEM analysis
on fresh and used clinoptilolite



- Typical "flake" structure: the particles appeared flat and assembled on the top of each other.
- The particles were characterized by grains with no well-defined crystal faces.
- After the adsorption of the metals, flatter and smoother surfaces appeared, more tidy in the case of zinc adsorption.
- Grains on surfaces were still present, smaller after cadmium adsorption.

- After adsorption process in binary system grains and flat surfaces were combined

CONCLUSIONS

- ✓ The capability of clinoptilolite as a low cost adsorbent for the removal of zinc and cadmium ions from wastewater was analyzed, exploiting its ion exchange property.
- ✓ Starting from a clinoptilolite concentration equal to 10 g/L, for both zinc and cadmium ions, complete adsorption was reached when the metal concentration in the solutions was very low.
- ✓ Increasing metals amount progressively, adsorption capacity decreased, most for Zn^{2+} .
- ✓ At maximum metal concentration of 200 mg/L, increasing clinoptilolite amount, the abatement was maintained over 60%.
- ✓ For all tests, the best performance was reached for Cd^{2+}, due to its ionic characteristics.
- ✓ Finally, adsorption tests in binary system were performed, showing a greater affinity of clinoptilolite towards Zn^{2+}, otherwise respect single metal system.
- ✓ Results in binary system confirmed literature data, as the zinc adsorption capacity was not influenced by cadmium presence while cadmium adsorption was reduced by zinc presence.

THANK YOU FOR THE ATTENTION!