
# Natural zeolite for the wastewater treatment

**Melodj Dosa, Nadia Grifasi, Camilla Galletti, Debora Fino and Marco Piumetti***

Department of Applied Science and Technology, Polytechnic of Turin, Turin, 10129, Italy.

20/06/2023- Chania

# *Table of content*

Water is one of the world's most valuable resources

recycle and reuse treated wastewater for beneficial purposes

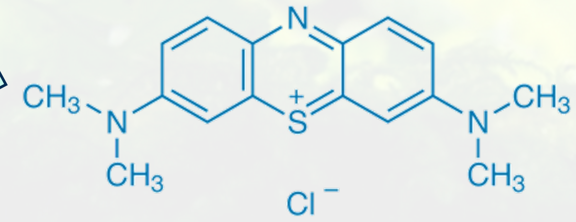
- agricultural
- industrial processes
- …

Wastewater treatment is essential to preserve public health and reduce levels of environmental degradation

Industrial effluents ⇒ main sources of water pollution

- **Synthetic organic dyes** ⇒ textile industry
- **Heavy metals** ⇒ mechanical and metallurgical processes

considered **micropollutants** due to their low concentration (ng/l to µg/l) in aquatic ecosystems.




Methylene Blue as organic dye probe molecule


Zn and Cd as heavy metals probe molecules

- high resistance to degradation
- high toxicity
- React with difficulty
- dangerous for human health


[1] Jhansi, S. C., & Mishra, S. K. (2013). Wastewater Treatment and Reuse: Sustainability Options. *Consilience*, *10*, 1–15.
[2] Tkaczyk, A., Mitrowska, K., & Posyniak, A. (2020). Synthetic organic dyes as contaminants of the aquatic environment and their implications for ecosystems: A review. *The Science of the total environment*, *717*, 137222.
[3] Dosa, M., Piumetti, M., Bensaid, S., Russo, N., Baglieri, O., Miglietta, F., & Fino, D. (2018). Properties of the Clinoptilolite: Characterization and Adsorption Tests with Methylene Blue.
[4] Galletti, C., Dosa, M., Russo, N. *et al.* $Zn^{2+}$ and $Cd^{2+}$ removal from wastewater using clinoptilolite as adsorbent. *Environ Sci Pollut Res* **28**, 24355–24361 (2021).

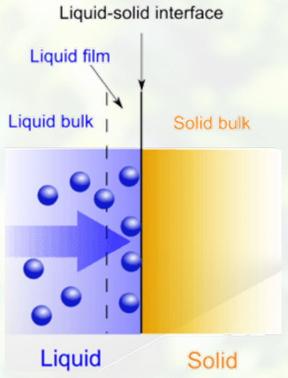
# Wastewater treatment technologies

Effective + simple to operate + low cost + environment-friendly

=

less energy positive impact

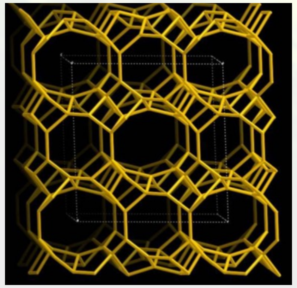
**Adsorption** is a highly effective technique for the removal of heavy metals and organic dyes from waste streams




effectiveness depends on

- size and porosity of surface area of adsorbent
- interaction between dye and adsorbent
- Temperature
- pH.

## CLINOPTILOLITE



$(NaKCa)_4(Al_6Si_{30}O_{72})\cdot 24H_2O$

- **low cost** and abudant **natural** zeolite
- found in basaltic and volcanic rocks
- interact with several compounds thanks to the presence of electrostatic forces into the cavities

⇩

suitable material for several environmental applications


[1] Jhansi, S. C., & Mishra, S. K. (2013). Wastewater Treatment and Reuse: Sustainability Options. *Consilience*, *10*, 1–15.
[2] Tkaczyk, A., Mitrowska, K., & Posyniak, A. (2020). Synthetic organic dyes as contaminants of the aquatic environment and their implications for ecosystems: A review. *The Science of the total environment*, *717*, 137222.
[4]Galletti, C., Dosa, M., Russo, N. *et al.* $Zn^{2+}$ and $Cd^{2+}$ removal from wastewater using clinoptilolite as adsorbent. *Environ Sci Pollut Res* **28**, 24355–24361 (2021).
[5] Diógenes, T. S., Santiago, R. G., Maia, D. A., Gonçalves, D. V., Azevedo, D. C., Lucena, S. M. P., & Bastos-Neto, M. (2022). Experimental and theoretical assessment of CO2 capture by adsorption on clinoptilolite. *Chemical Engineering Research and Design*, *177*, 640-652.

**Characterization**

# Adsorbent materials were characterized to describe their physical-chemical properties

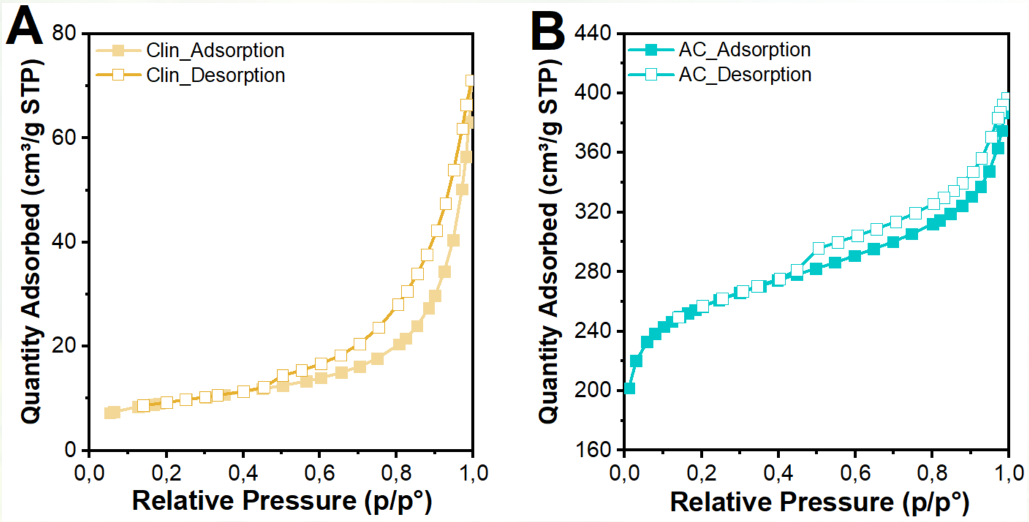



**Fig.1** $N_2$ adsorption/desorption isotherms at − 196 °C for Clin (A) and AC (B)

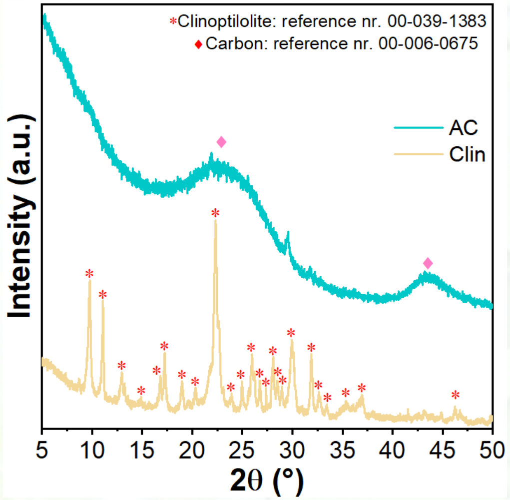



**Fig.2** X-ray diffractograms in the range 5°< 2θ < 50° over Clin and AC.

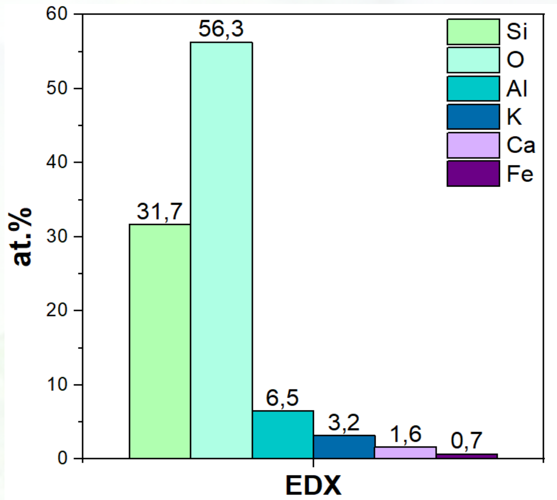



**Fig.3** Chemical composition of Clin evaluated by the EDX analysis

**Table 1.** Specific Surface Area (SSA), Total Pores Volume ($V_{TP}$), and Pores Diameter ($D_P$) of the Clin and AC samples

| Adsorbent material | SSA ($m^2g^{-1}$) | $V_{TP}$ ($cm^3g^{-1}$) | $D_p$ |
|---|---|---|---|
| Clin | 32 | 0.12 | A channel 3.0 x 7.6 Å<br>B channel 3.3 x 4.6 Å<br>C channel 2.6 x 4.7 Å |
| AC | 891 | 0.56 | 3.3 nm |

- Clin → high crystallinity

Main peaks at
- 9.92° (0 2 0)
- 11.09° (2 0 0)
- 22.43° (1 3 1)

- AC → low crystallinity

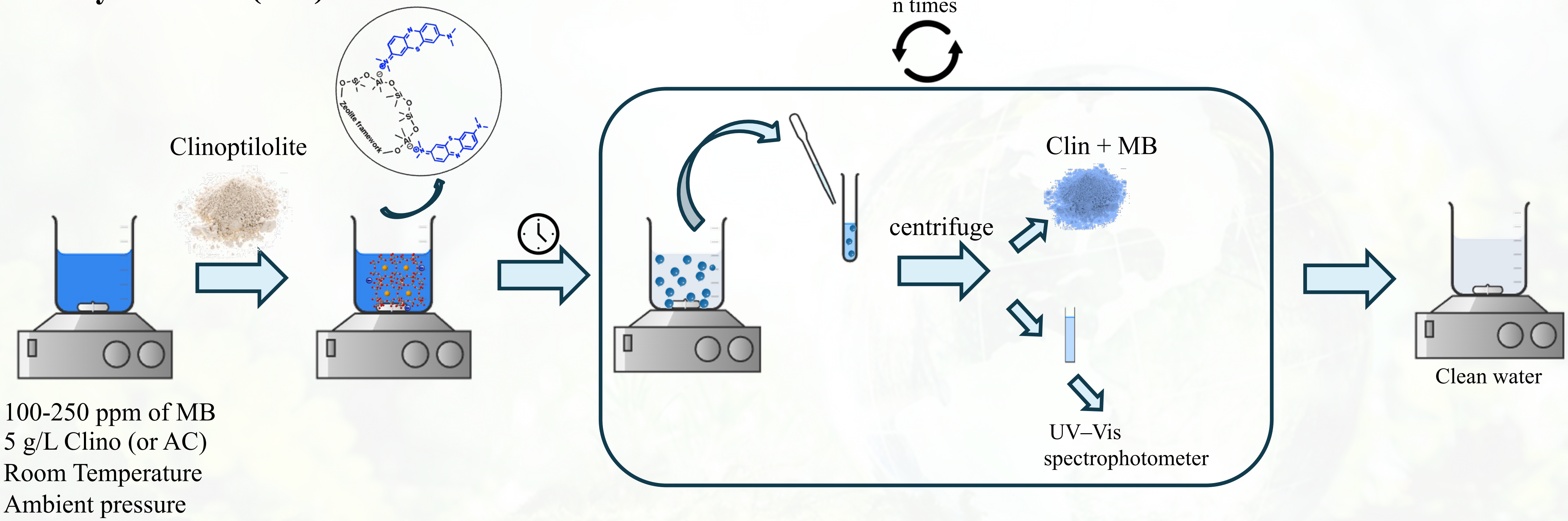
main peaks at
- 22.56° (0 0 2)
- 43.57° (1 0 1)

- Si and Al → main elements
- K, Ca and Fe → minimum quantity

[6] Dosa, M.; Grifasi, N.; Galletti, C.; Fino, D.; Piumetti, M. Natural Zeolite Clinoptilolite Application in Wastewater Treatment: Methylene Blue, Zinc and Cadmium Abatement Tests and Kinetic Studies. *Materials* **2022**, *15*, 8191.
[7] Dosa, M., Piumetti, M., Davarpanah, E., Moncaglieri, G., Bensaid, S., Fino, D. (2021). Natural Zeolites as Sustainable Materials for Environmental Processes. In: Piumetti, M., Bensaid, S. (eds) Nanostructured Catalysts for Environmental Applications. Springer, Cham. https://doi.org/10.1007/978-3-030-58934-9_13

## *Adsorption tests*

### ❑ Methylene Blue (MB) abatement test




### ❑ Co-presence of Methylene blue and Heavy metals (Zn, Cd) abatement test

$Cd(NO_3)_2 \cdot 4H_2O$ and $ZnSO_4 \cdot 7H_2O$ as metal source

250 ppm of MB, 10 ppm heavy metals, 10 g/L Clino (or AC)

$Zn^{2+}$ and $Cd^{2+}$ → Inductively Coupled Plasma-Mass Spectrometer (iCAP Q ICP-MS)


[6] Dosa, M.; Grifasi, N.; Galletti, C.; Fino, D.; Piumetti, M. Natural Zeolite Clinoptilolite Application in Wastewater Treatment: Methylene Blue, Zinc and Cadmium Abatement Tests and Kinetic Studies. *Materials* **2022**, *15*, 8191.

## ❑ Methylene Blue adsorption results at different concentrations

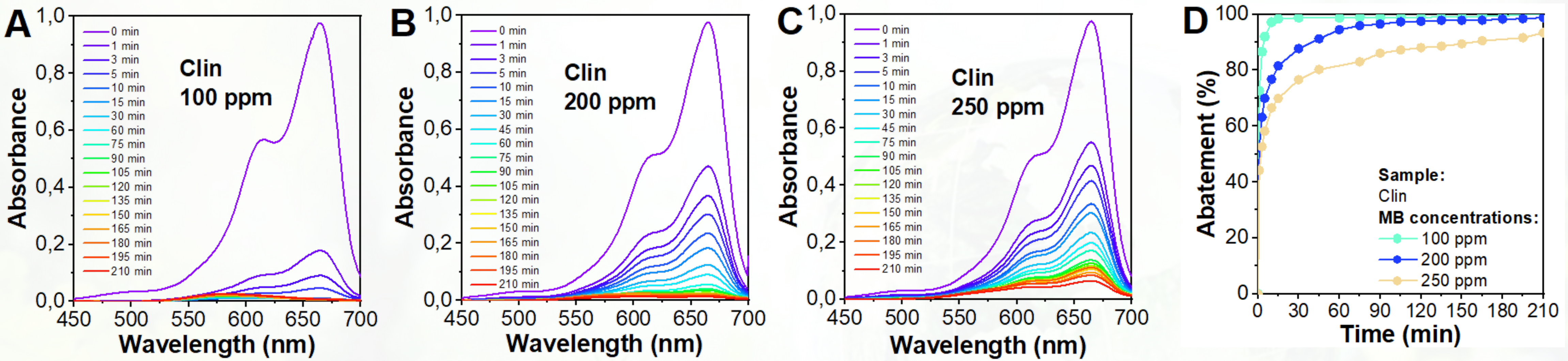



**Fig.6** Clin (5 g/L) abatement tests performed with 100 ppm (A), 200 ppm (B), and 250 ppm (C) MB concentrations and MB abatement as a function of time (D)

- ✓ active adsorption sites on zeolite surface → silanol groups
- ✓ MB pKa = 3.80 ⇨ MB exists as a molecular cation in water @ pH > 4

MB removal capacity → electrostatic interaction between MB cation and surface silanol groups

pH ⇩ repulsive interaction between the protonated groups ($Si\text{-}OH_2^+$) and cationic MB

pH ⇧ attractive interaction between the deprotonated groups ($Si\text{-}O^-$) and cationic MB

after 210 min

100 ppm ⇨ 100%
200 ppm ⇨ 99%
250 ppm ⇨ 93%

**Table 2.** pH values at the beginning of MB abatement tests

| Adsorbent Material | MB Concentration (ppm) | pH $\|_{time=0\ min}$ |
|---|---|---|
| Clin | 100 | 8.36 |
| | 200 | 8.01 |
| | 250 | 6.18 |

Additionally, MB adsorption could be performed by cationic exchange and coordination with the oxygen donor atoms of the zeolite surface.

[6] Dosa, M.; Grifasi, N.; Galletti, C.; Fino, D.; Piumetti, M. Natural Zeolite Clinoptilolite Application in Wastewater Treatment: Methylene Blue, Zinc and Cadmium Abatement Tests and Kinetic Studies. *Materials* **2022**, *15*, 8191.
[8] Picón, D.; Vergara-Rubio, A.; Estevez-Areco, S.; Cerveny, S.; Goyanes, S. Adsorption of Methylene Blue and Tetracycline by Zeolites Immobilized on a PBAT Electrospun Membrane. *Molecules* **2023**, *28*, 81.

## ❑ Methylene Blue adsorption results over Clin and AC

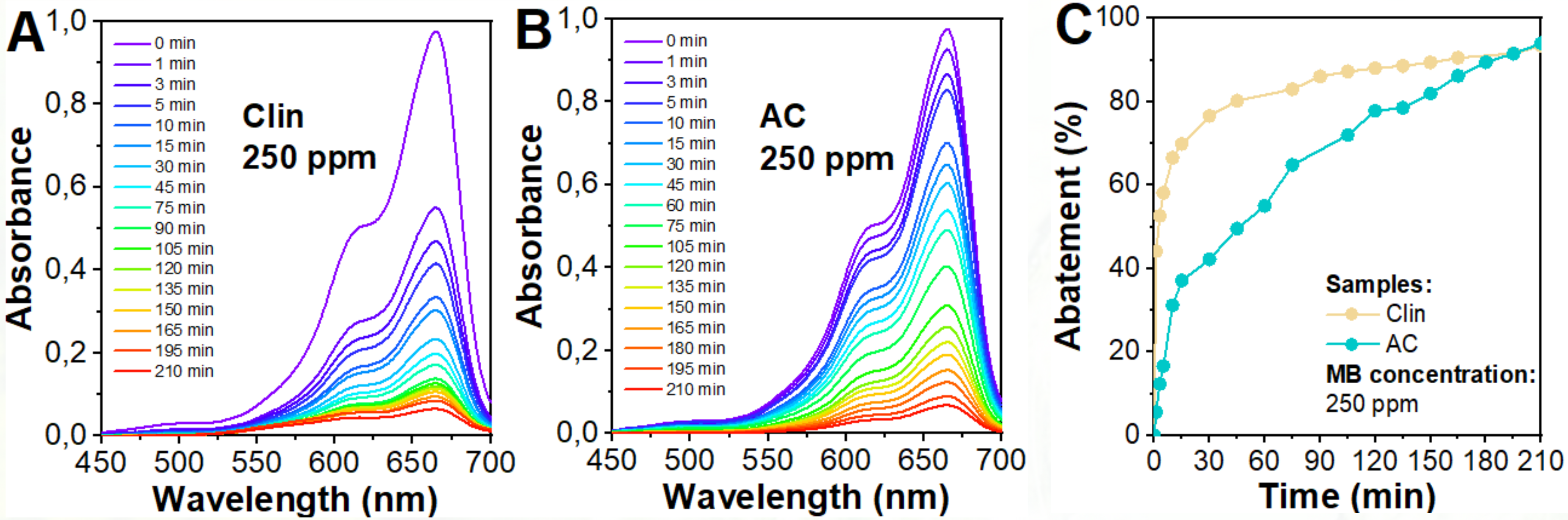



**Fig.7** Clin (5 g/L) abatement tests (A) and AC (5 g/L) (B) performed with 250 ppm MB. MB abatement as a function of time (C) at 250 ppm MB

after 210 min

Clin ⇨ 93%

AC ⇨ 94%

- MB easily attracted on the Clin surface ⇨ presence of metal cations on the Clin surface; good ion-exchange properties

- AC active sites

carboxyl, lactone, lactol, phenol, carbonyl, anhydride, ether, quinone, pyrone, chromene, pyridine, quaternary, pyridine, oxidized N, and pyrrole groups.

⇨ partial hydration of such chemical groups in water

⇩

NO strong interaction with cationic MB

[6] Dosa, M.; Grifasi, N.; Galletti, C.; Fino, D.; Piumetti, M. Natural Zeolite Clinoptilolite Application in Wastewater Treatment: Methylene Blue, Zinc and Cadmium Abatement Tests and Kinetic Studies. *Materials* **2022**, *15*, 8191.

❑ Adsorption results over Clin and AC with **co-presence** of **Methylene Blue and heavy metals**

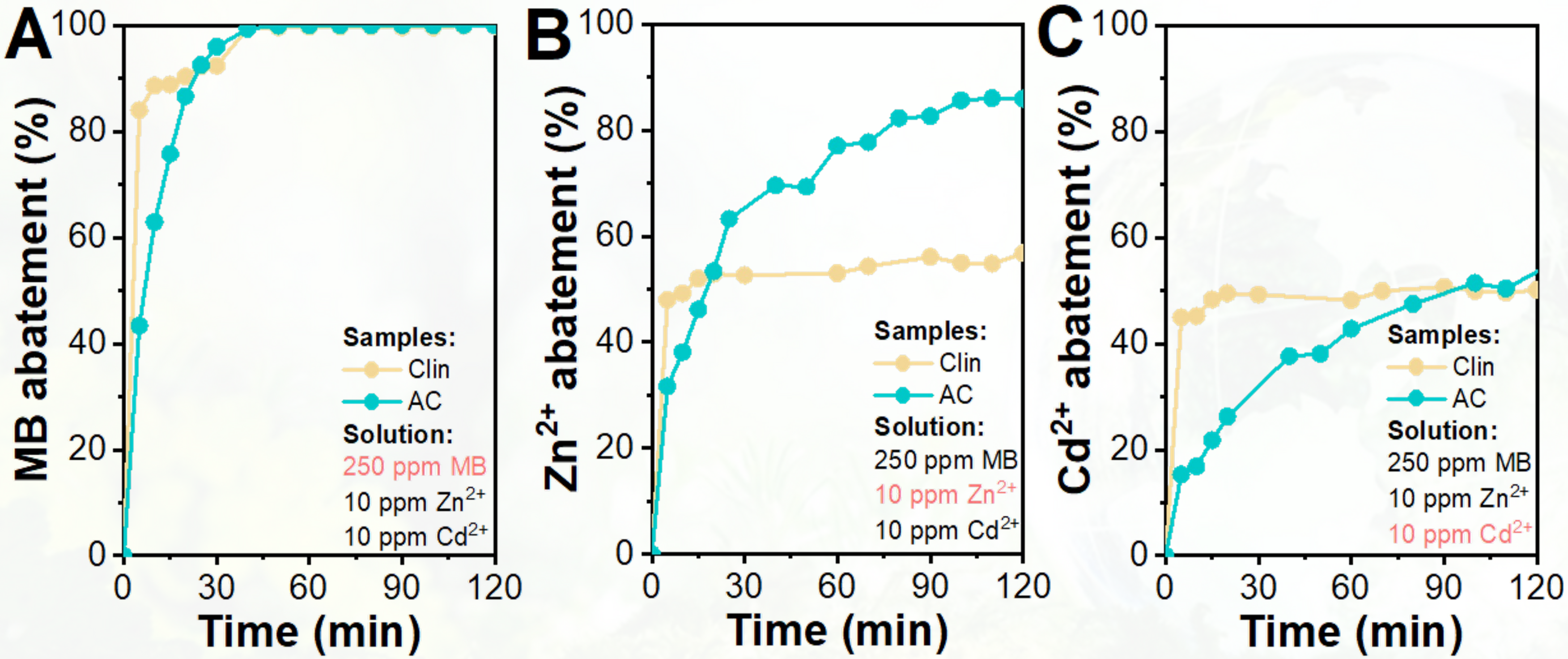



**Fig.8** Clin and AC abatement tests (10 g/L) with 250 ppm MB (A), 10 ppm $Zn^{2+}$ (B), and 10 ppm $Cd^{2+}$ (C) as a function of time.

after 120 min

Clin

⇩

100% MB, 57% $Zn^{2+}$, 50% $Cd^{2+}$

AC

⇩

100% MB, 86% $Zn^{2+}$, 53% $Cd^{2+}$

- preferential adsorption of MB on the Clin surface
- adsorption of divalent cations with high hydration energy is nonselective
- adsorption of both metal cations reached a plateau
- $Zn^{2+}$ is preferentially adsorbed instead of $Cd^{2+}$ ⇨ ionic radii Cd (0.97 Å) > Zn (0.74 Å)

[6] Dosa, M.; Grifasi, N.; Galletti, C.; Fino, D.; Piumetti, M. Natural Zeolite Clinoptilolite Application in Wastewater Treatment: Methylene Blue, Zinc and Cadmium Abatement Tests and Kinetic Studies. *Materials* **2022**, *15*, 8191.

## ABATEMENT KINETIC

Models most commonly used to describe the sorption of dyes as well as other pollutants (heavy metals) on solid sorbents

Starting from the linearization

⇩

estimate model parameters from the slope and the intercept

- *Pseudo First Order (PFO)*

$$\frac{dq}{dt} = k_1 \cdot (q_e - q) \quad (1)$$

- *Pseudo Second Order (PSO)*

$$\frac{dq}{dt} = k_2 \cdot (q_e - q)^2 \quad (2)$$

- *Elovich model*

$$\frac{dq}{dt} = \alpha \cdot exp(-\beta \cdot q) \quad (3)$$

- *Intraparticle diffusion model*

$$q_t = k_i \cdot t^{0.5} + C \quad (4)$$

- *Bangham model*

$$ln(q_t) = \vartheta \cdot ln(t) + ln(k_B) \quad (5)$$

- *Avrami kinetic model*

$$\frac{dq}{dt} = k \cdot n \cdot t^{n-1} \cdot (q_e - q) \quad \text{with } n \neq 1 \quad (6)$$

[6] Dosa, M.; Grifasi, N.; Galletti, C.; Fino, D.; Piumetti, M. Natural Zeolite Clinoptilolite Application in Wastewater Treatment: Methylene Blue, Zinc and Cadmium Abatement Tests and Kinetic Studies. *Materials* **2022**, *15*, 8191.

## ❑ Abatement kinetics: Pseudo Second Order Model (PSO)

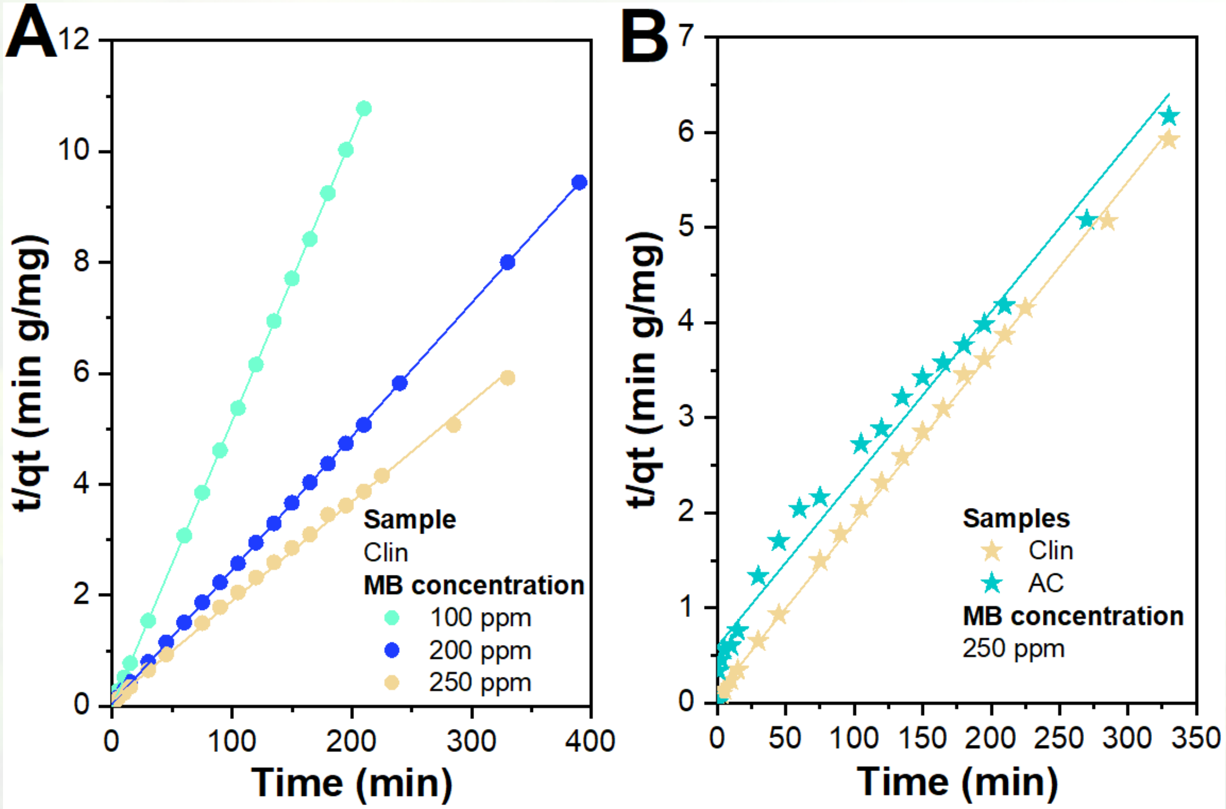



**Fig.9** Experimental data of MB abatement tests fitted with a PSO kinetic model with different concentrations of MB on Clin (A) and by using 250 ppm MB on Clin and AC (B).

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

**Table 3.** Kinetic parameters of MB abatement using Clin and AC as adsorbents.

| | MB concentration (ppm) | | | |
|---|---|---|---|---|
| | Clin | | | AC |
| parameter | 100 | 200 | 250 | 250 |
| $R^2$ | 1 | 1 | 0.9985 | 0.9786 |
| $k_2$ [g mg$^{-1}$ min$^{-1}$] | 0.4460 | 0.0127 | 0.0033 | 0.0005 |
| qe, fit [mg g$^{-1}$] | 19.4932 | 41.4938 | 55.5556 | 56.8182 |
| qe, exp [mg g$^{-1}$] | 19.5897 | 41.4197 | 56.2159 | 53.5020 |

PSO equation represents the adsorption kinetic of both contaminants more accurately ➡ highest coefficient of determination $R^2$

According to the model ➡ **chemisorption** is the primary mechanism involved in the adsorption of pollutants.

[6] Dosa, M.; Grifasi, N.; Galletti, C.; Fino, D.; Piumetti, M. Natural Zeolite Clinoptilolite Application in Wastewater Treatment: Methylene Blue, Zinc and Cadmium Abatement Tests and Kinetic Studies. *Materials* **2022**, *15*, 8191.

## ❑ Abatement kinetics: Pseudo Second Order Model (PSO)

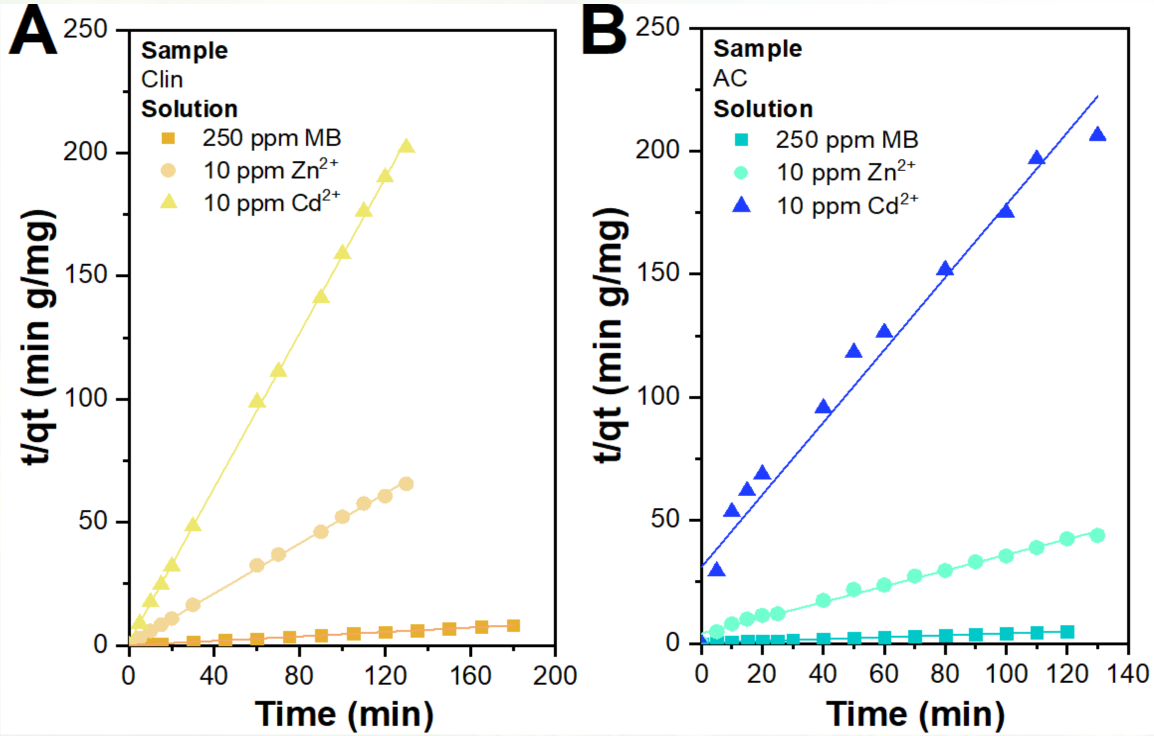



**Fig.10** Experimental data of a system with 250 ppm MB, 10 ppm $Zn^{2+}$, and 10 ppm $Cd^{2+}$ fitted with a PSO kinetic model by using Clin (A) and AC (B) as adsorbents.

**Table 4.** Kinetic parameters of the system with 250 ppm MB, 10 ppm $Zn^{2+}$, and 10 ppm $Cd^{2+}$, using Clin and AC as adsorbents.

| | $C_{MB}$=250 ppm; $C_{Zn}$=10 ppm; $C_{Cd}$= 10 ppm | | | | | |
|---|---|---|---|---|---|---|
| | Clin | | | AC | | |
| **Parameters** | **MB** | **Zn** | **Cd** | **MB** | **Zn** | **Cd** |
| $R^2$ | **0.9999** | **0.9990** | **0.9995** | **0.9979** | **0.9902** | **0.9631** |
| $k_2$ | 0.0609 | 0.3228 | 1.8599 | 0.0108 | 0.0253 | 0.0699 |
| $q_{e,fit}$ | 22.2717 | 1.9716 | 0.6370 | 25.3807 | 3.1279 | 0.6797 |
| $q_{e,exp}$ | 22.2054 | 1.9820 | 0.6430 | 24.4256 | 2.968 | 0.6300 |

the PSO kinetic model exhibited the best fit over the entire time range for both adsorbents tested confirming chemisorption control over the entire abatement process.

- ✓ $R^2$ coefficient close to unity
- ✓ values of $q_{e,fit}$ and $q_{e,exp}$ similar to each other

[6] Dosa, M.; Grifasi, N.; Galletti, C.; Fino, D.; Piumetti, M. Natural Zeolite Clinoptilolite Application in Wastewater Treatment: Methylene Blue, Zinc and Cadmium Abatement Tests and Kinetic Studies. *Materials* **2022**, *15*, 8191.

## *Conclusion*

**chemisorption** is the primary mechanism involved in the adsorption of pollutants.

a highly effective material for the **removal of heavy metals and organic dyes** from waste streams

suitable material for several **environmental applications** thanks to different composition

**Abundant** and easy to find in nature

Valid and **sustainable alternative** to expensive adsorbent

less energy
positive impact

6 CLEAN WATER AND SANITATION

# *Acknowledgments*

Zeolado Company is fully acknowledged for providing the Clinoptilolite used in this study
Alessandra Gatto and Veronica Comodin for performing the adsorption tests

***Thank you for your kind attention***

Nadia Grifasi
PhD student in Chemical Engineering
e-mail: nadia.grifasi@polito.it
Department of Applied Science and Technology
Polytechnic of Turin

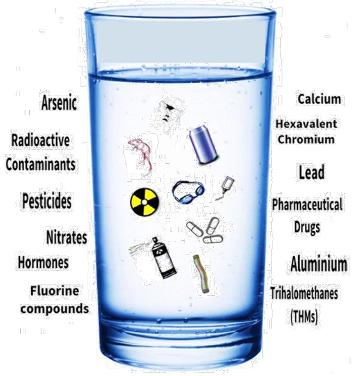
# ***Supporting information***

The most popular and widespread industrial pollutants include:

- Asbestos
- Heavy metals
- Petrochemical
- Pharmaceuticals
- synthetic organic dyes
- pesticides

→

- carcinogenic
- non-biodegradable
- inhibit the action of bodily enzymes
- problematic for marine environments




[1] Jhansi, S. C., & Mishra, S. K. (2013). Wastewater Treatment and Reuse: Sustainability Options. *Consilience*, *10*, 1–15.
[2] Tkaczyk, A., Mitrowska, K., & Posyniak, A. (2020). Synthetic organic dyes as contaminants of the aquatic environment and their implications for ecosystems: A review. *The Science of the total environment*, *717*, 137222.

Synthetic organic dyes and heavy metals are considered **micropollutants** due to their low concentration (ng/l to µg/l) in aquatic ecosystems.

- **Synthetic organic dyes** ➡ textile industry

- non-biodegradable

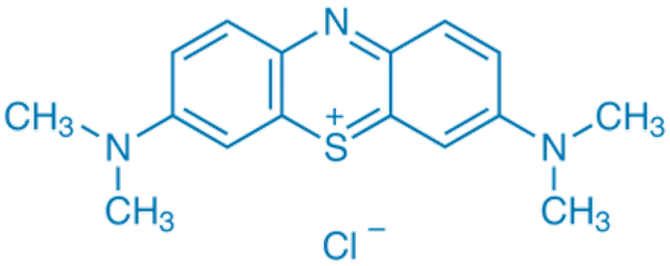
wastewater more difficult to clean up by commercial methods

- toxic properties

carcinogenic, allergic and dermatics effects

- react with difficulty

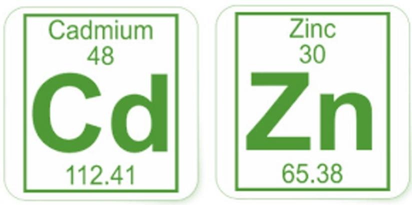
stable to light, resistant to aerobic digestion and heat.




Methylene Blue as probe molecule

- **Heavy metals** ➡ mechanical and metallurgical processes

- high resistance to degradation
- high toxicity
- tend to accumulate in the environment
- exposure is very dangerous for human health

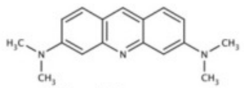
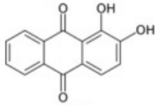
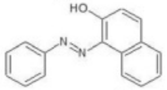
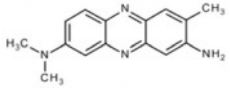
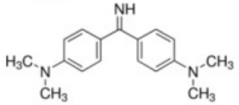
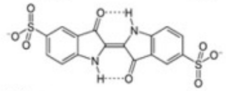
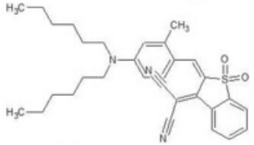
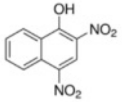
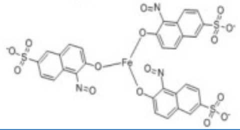
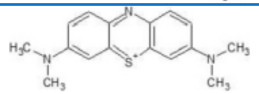




[2] Tkaczyk, A., Mitrowska, K., & Posyniak, A. (2020). Synthetic organic dyes as contaminants of the aquatic environment and their implications for ecosystems: A review. *The Science of the total environment*, *717*, 137222.
[3] Dosa, M., Piumetti, M., Bensaid, S., Russo, N., Baglieri, O., Miglietta, F., & Fino, D. (2018). Properties of the Clinoptilolite: Characterization and Adsorption Tests with Methylene Blue.
[4] Galletti, C., Dosa, M., Russo, N. *et al.* $Zn^{2+}$ and $Cd^{2+}$ removal from wastewater using clinoptilolite as adsorbent. *Environ Sci Pollut Res* **28**, 24355–24361 (2021).

# ❑ SYNTHETIC ORGANIC DYES

The main classes of synthetic organic dyes and their examples based on their chromogens.

| Chromogen | Colour index Generic name/colour Index Constitution number | CAS No. | Common name | Structural formula of dye | $\lambda_{max}$ [nm] |
|---|---|---|---|---|---|
| Acridine | C.I. basic orange 14<br>C.I. 46005 | 10127-02-3 | Acridine orange |  | 500 |
| Anthraquinone | C.I. mordant red 3<br>C.I. 58005 | 72-48-0 | Alizarin red s |  | 609 |
| Azo | C.I. solvent yellow 14<br>C.I. 12055 | 842-07-9 | Sudan I |  | 476 |
| Azine | C.I. basic red 5<br>C. I. 50040 | 553-24-2 | Neutral red |  | 530 |
| Diphenylmethane | C.I. basic yellow 2<br>C.I. 41000 | 2465-27-2 | Auramine O |  | 432 |
| Indigoid | C.I. acid blue 74<br>C.I. 73015 | 860-22-0 | Indigo carmine |  | 612 |
| Methine | C.I. disperse blue 354<br>C.I. 48480 | 104137-27-1 | |  | 610 |
| Nitro | C.I. acid yellow 24<br>C. I. 10315 | 605-69-6 | Martius yellow |  | 432 |
| Nitroso | C.I. acid green 1<br>C.I. 10020 | 19381-50-1 | Naphthol green B |  | 714 |
| Thiazine | C.I. basic blue 9<br>C.I. 52015 | 61-73-4 | Methylene blue |  | 660 |

List of the synthetic organic dyes determined in different types of effluent and sewagee sludge.

| Dye name | Type of wastewater | Analytical method[a] | Limit of detection [μg/kg or μg/l] | Limit of quantitation [μg/kg or μg/l] | Concentration determined [μg/kg or μg/l] | Reference |
|---|---|---|---|---|---|---|
| Malachite green | Fish farm effluent | LC – MS | ND[b] | ND | 0.0057–0.384 | (Khodabakhshi and Amin, 2012) |
| Acid yellow 15 | STP effluent | HPLC – UV | ND | ND | Σ:2–3750 | (Tincher, 1978) |
| Acid red 337 | | | | | | |
| Acid yellow 19 | | | | | | |
| Acid yellow 135 | | | | | | |
| Acid orange 128 | | | | | | |
| Acid red 151 | | | | | | |
| Acid blue 25 | | | | | | |
| Acid blue 40 | | | | | | |
| Disperse yellow 3 | | | | | | |
| Disperse yellow 23 | | | | | | |
| Disperse yellow 54 | | | | | | |
| Disperse red 55 | | | | | | |
| Disperse red 60 | | | | | | |
| Disperse blue 7 | | | | | | |
| Disperse blue 120 | | | | | | |
| Acid red 1 | STP effluent | HPLC – MS | 0.002 | ND | 0.80–1.19 | (Loos et al., 2003) |
| Disperse blue 14 | | | | | 0.021–2.34 | |
| Disperse red 1 | | | | | 0.054–0.207 | |
| Sulphorhodamine B | | | | | 0.09–8.21 | |
| Rhodamine 6G | STP effluent | HPLC – FLD | 0.0001 | 0.0003 | 0.0007 | (Chiang et al., 2011) |
| Rhodamine B | | | 0.0005 | 0.0015 | 0.037–0.062 | |
| Disperse red 1 | STP effluent | HPLC – MS/MS | 0.002 | 0.008 | 0.15 | (Zocolo et al., 2015) |
| Disperse blue 373 | | | | | 1.13–1.47 | |
| Disperse violet 93 | | | | | 0.79–1.47 | |
| Disperse blue 291 | STP effluent | HPLC – MS/MS | 0.0022 | 0.0075 | 0.05 | (Vacchi et al., 2017) |
| Disperse blue 373 | | | 0.0016 | 0.0054 | 0.08–0.35 | |
| Disperse red 1 | | | 0.0003 | 0.0010 | 0.03–0.19 | |
| Disperse blue 373 | Textile effluent untreated/textile effluent treated | HPLC – DAD | ND | ND | 57.9/67 | (Oliveira et al., 2007) |
| Disperse orange 37 | | | | | 316/126 | |
| Disperse orange 37 | Textile effluent untreated/textile effluent treated | HPLC – DAD | 0.09[c] | 0.27[c] | 316/126 | (Carneiro et al., 2010) |
| Disperse violet 93 disperse blue 373 | | | 0.84[c]<br>0.09[c] | 0.84[c]<br>0.26[c] | 12/6.03<br>57.9/67 | |
| Disperse brown 1 | Textile effluent | SFC – UV | 2.9 | 9.6 | 109 | (Lou et al., 2018) |
| Disperse orange 3 | | | 1.9 | 6.2 | 17 | |
| Disperse orange 37/76 | | | 4.0 | 13.5 | 53 | |
| Disperse red 1 | | | 1.1 | 3.7 | 12–34 | |
| Disperse red 17 | | | 3.3 | 11 | 63 | |
| Disperse yellow 1 | | | 15.6 | 52 | 90–306 | |
| Disperse yellow 49 | | | 3.1 | 10.5 | 23–428 | |
| Brilliant green | Textile wastewater | UV–vis | 47 | ND | 3220 | (Damirchi et al., 2019) |
| Methylene blue | Laundry effluent | UPLC – MS/MS | 0.3 | 0.9 | 360 | (Khan et al., 2014) |
| | Paper effluent | | | | 540 | |
| | Printing effluent | | | | 830 | |
| | Textile effluent | | | | 1080 | |
| Malachite green | Laundry effluent | UPLC – MS/MS | 0.1 | 0.4 | 1320 | (Khan et al., 2019) |
| | Paper effluent | | | | 620 | |
| | Printing effluent | | | | 790 | |
| | Textile effluent | | | | 1680 | |

The textile industry is an important source of dyes in water environments: during different dyeing processes dye wastage is at least 5% and can reach 50%, depending on the type of fabric and dye and as a result almost 200 billion litres of coloured effluents are generated annually. It is estimated that 2% of dyes produced are discharged directly into the blow-down system


[2] Tkaczyk, A., Mitrowska, K., & Posyniak, A. (2020). Synthetic organic dyes as contaminants of the aquatic environment and their implications for ecosystems: A review. *The Science of the total environment*, *717*, 137222.
[3] Dosa, M., Piumetti, M., Bensaid, S., Russo, N., Baglieri, O., Miglietta, F., & Fino, D. (2018). Properties of the Clinoptilolite: Characterization and Adsorption Tests with Methylene Blue.

Heavy metals in some major industries

| Industry source | Al | Zn | As | Sn | Ag | Sb | Cd | Cr | Cu | Fe | Hg | Mn | Pb | Ni | Bi |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Automobile | | X | | X | | | X | X | | X | | | X | X | |
| Petroleum refining | | X | X | | | | | X | X | X | | | X | X | |
| Pulp and paper | | X | | | | | | X | X | | X | | X | X | |
| Textile | | | | | | | | X | | | | | | | |
| Steel | | X | X | | | X | X | X | | X | | | X | X | |
| Organic chemicals | X | X | X | X | | | X | X | | X | X | | X | | |
| Inorganic chemicals | X | X | X | | | | X | X | | X | X | | X | | |
| Fertilizer | X | X | X | | | | X | X | X | X | X | X | X | X | |
| Plastic and synthetics | | | | | | | | | | X | | | | | |
| Leather tanning and finishing | | | | | | | | X | | | | | | | |
| Steel power plants | | X | | | | | | X | | | | | | | |
| Mining | | | X | | | | X | | X | | X | X | X | | |
| Acid mine drainage | X | X | | | | | | | X | X | | X | | | |
| Metal plating | | X | | | | | X | X | X | | | | | | |
| Glass | | | X | | | | | | | | | | | | |
| Nuclear power | | | | | | | | | | | | | | | X |
| Coal and gasoline | | | | | | | | | | | X | | X | | X |

- Zinc

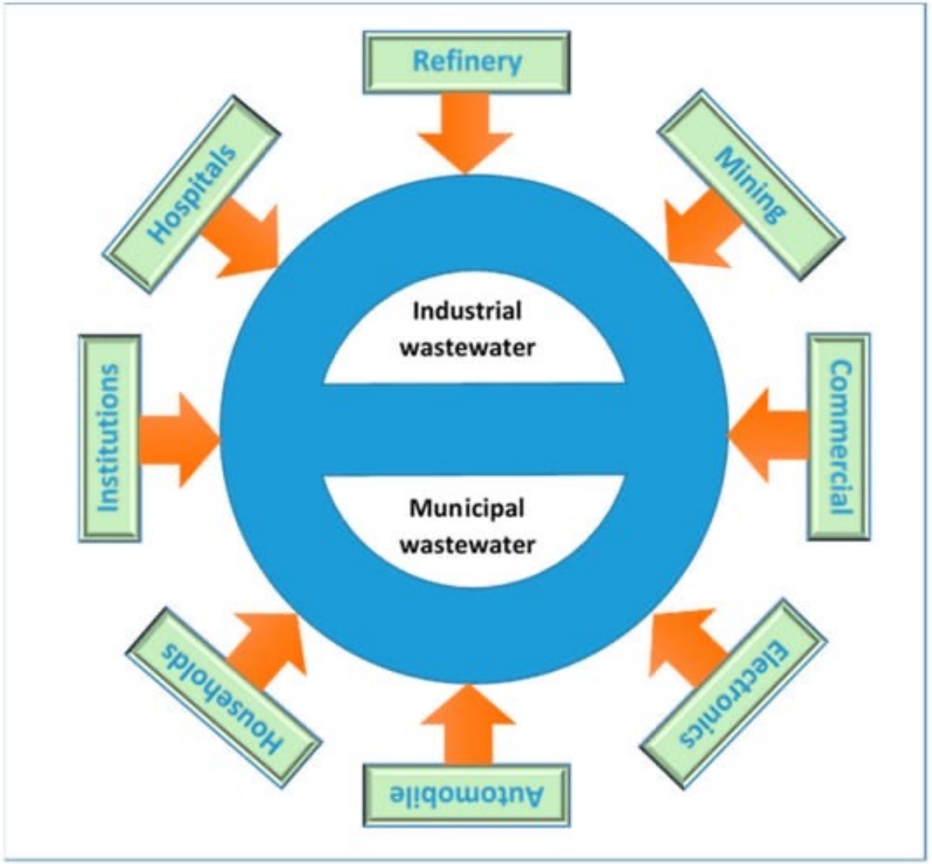
galvanic process

- Cadmium

nickel–cadmium batteries, pigments, coatings, and stabilizers for plastic materials



Mohan, D., & Pittman, C. U., Jr (2006). Activated carbons and low cost adsorbents for remediation of tri- and hexavalent chromium from water. *Journal of hazardous materials*, *137*(2), 762–811.




Depicts a schematic representation of industrial and municipal wastewater sources[9]


Main techniques used in wastewater purification [10]

[9] El Batouti, M.; Al-Harby, N.F.; Elewa, M.M. A Review on Promising Membrane Technology Approaches for Heavy Metal Removal from Water and Wastewater to Solve Water Crisis. *Water* **2021**, *13*, 3241.
[10] Rafique, M., Hajra, S., Tahir, M. B., Gillani, S. S. A., & Irshad, M. (2022). A review on sources of heavy metals, their toxicity and removal technique using physico-chemical processes from wastewater. *Environmental Science and Pollution Research*, *29*(11), 16772-16781.

# ❑ ACTIVATED CARBON

Advantages and disadvantages of commercial activated carbons

| Adsorbent | Advantages | Disadvantages |
| --- | --- | --- |
| Activated carbon | • The most effective adsorbent<br>• Very high surface areas<br>• Porous sorbent<br>• High capacity and high rate of adsorption<br>• Great capacity to adsorb a wide range of pollutants<br>• Fast kinetics<br>• A high quality-treated effluent is obtained | • Expensive<br>• The higher the quality, the greater the cost<br>  • Performance is dependent on the type of carbon used<br>  • Requires complexing agents to improve its removal performance<br>• Non-selective<br>• Problems with hydrophilic substances<br>• Ineffective for disperse and vat dyes<br>• High reactivation costs<br>• Reactivation results in a loss of the carbon |

The most effective adsorbent is activated carbon but due to a high cost other inexpensive adsorbents are employed sourced from different types of wastes such as bamboo, coir pith, oil palm shell or rubber tire.

Mohan, D., & Pittman, C. U., Jr (2006). Activated carbons and low cost adsorbents for remediation of tri- and hexavalent chromium from water. *Journal of hazardous materials*, *137*(2), 762–811.
Dosa, M.; Grifasi, N.; Galletti, C.; Fino, D.; Piumetti, M. Natural Zeolite Clinoptilolite Application in Wastewater Treatment: Methylene Blue, Zinc and Cadmium Abatement Tests and Kinetic Studies. *Materials* **2022**, *15*, 8191.

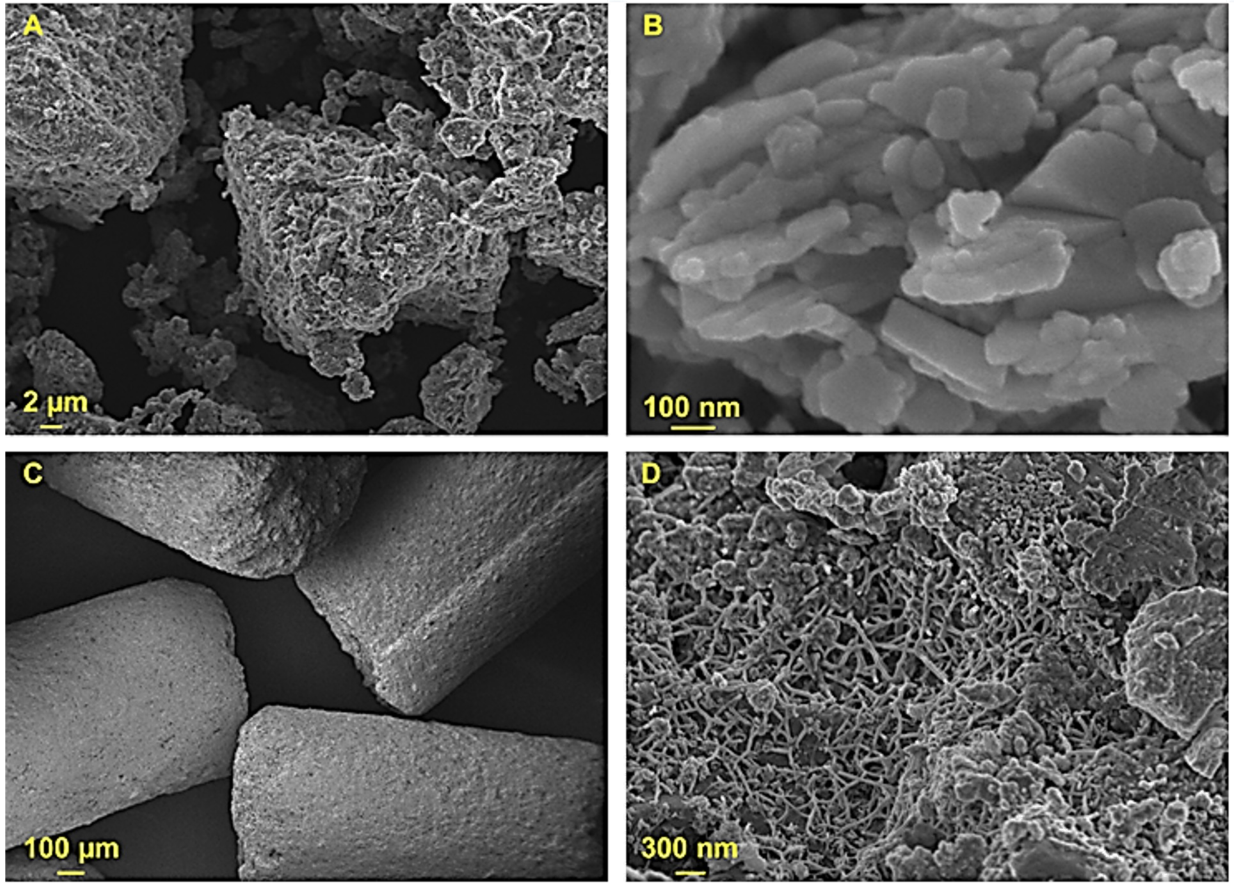



**Fig.4** FESEM images of Clin (A,B) and AC (C,D) at different magnifications

- Clin exhibits flake-like structure and grains with no well-defined crystal faces (A, B)
- AC presents a multiwallet mesopore structure (C,D)

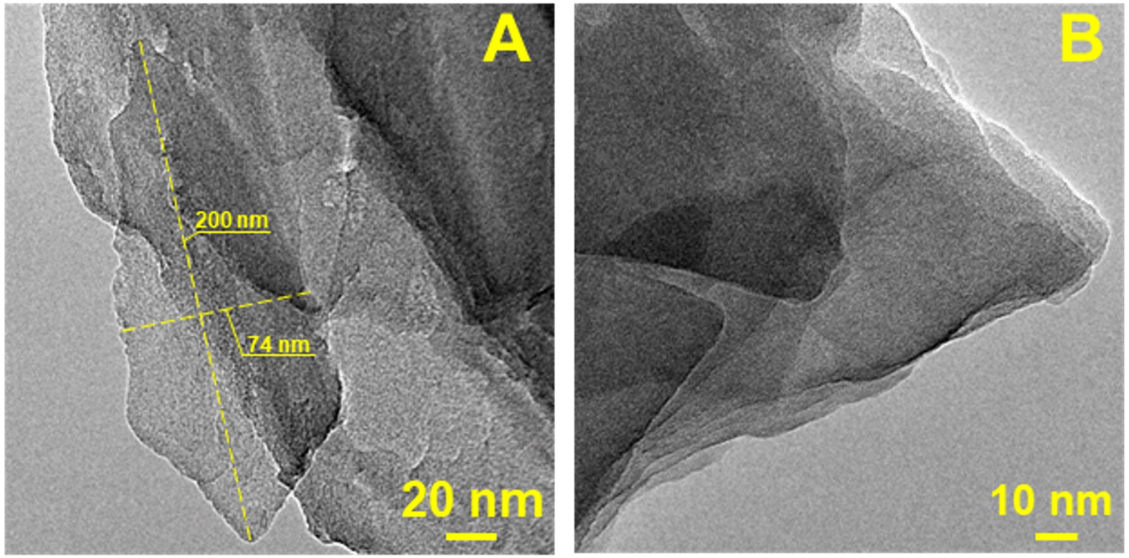
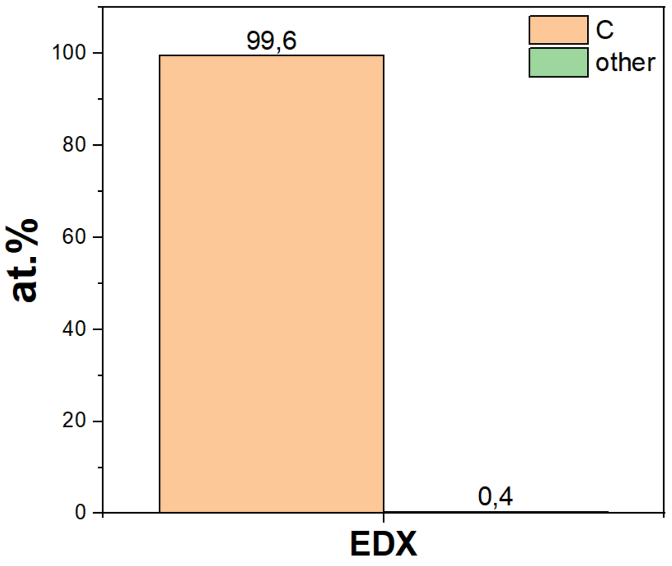



**Fig.5** TEM images of Clin at two different magnifications, (A) 20 nm and (B) 10 nm.

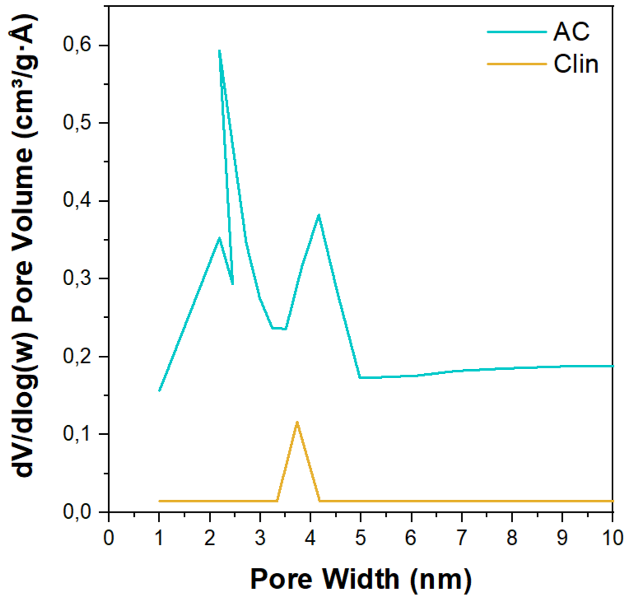
- flake-like structure of Clin
- average dimension of a particular Clin particle → 200 × 74 nm

[6] Dosa, M.; Grifasi, N.; Galletti, C.; Fino, D.; Piumetti, M. Natural Zeolite Clinoptilolite Application in Wastewater Treatment: Methylene Blue, Zinc and Cadmium Abatement Tests and Kinetic Studies. *Materials* **2022**, *15*, 8191.

# ❑ ACTIVATED CARBON: composition and PSD




Elemental composition of AC




PSD from BJH

- black granules with an average dimension of particles (≤0.5%) less than 0.60 mm.
- The water content, evaluated by the Karl Fisher Titration method, was lower than 0.5%.
- Steam activated

Methylene blue (MB) :
volume of dimensions 17.0 x 7.6 x 3.3 Å

## ❑ PRICE OF CLIN AND ACTIVATED CARBON

ACTIVATED CARBON → price changes depending on the procedure and the matrix used

The prices for **clinoptilolite** zeolite typically range from **$200 to $600 per tons**, depending on several factors, including the zeolite content and processing, origin and market prices

Overall, the costs of **AC** are approximately **1.08–2.89 $ kg−1**.

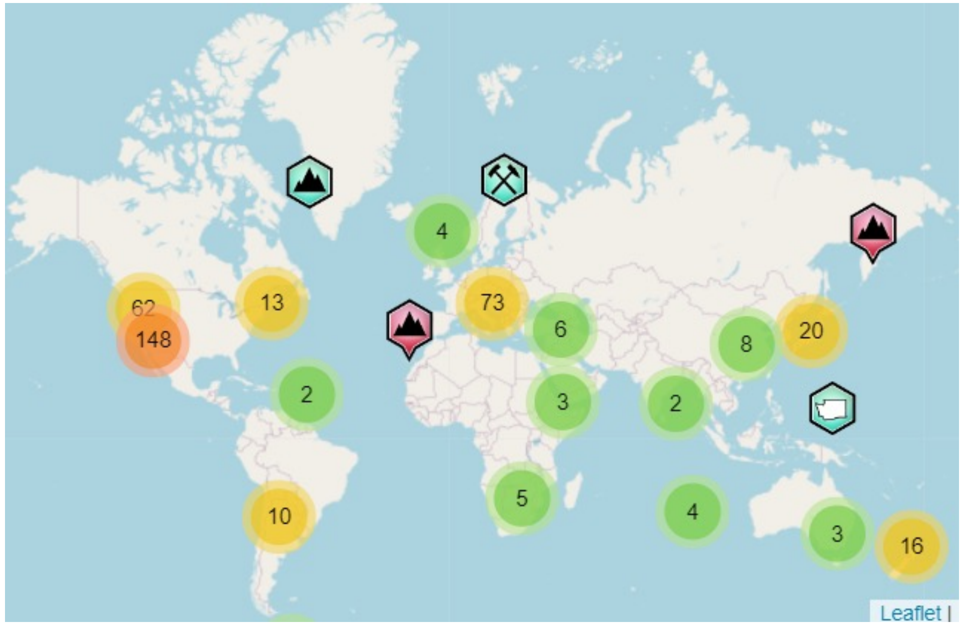
Thus, it is evident that Clin is cheaper than AC

| Matrix | Cost (USD $kg^{-1}$) |
|---|---|
| Pecan shell | 2.72-2.89 |
| Poultry waste | 1.44 |
| Tires | 2.23 |
| Wood, | 2.49 |
| Petroleum coke | 1.08 |
| Carbon black | 1.22 |
| Coal | 1.25 |
| Lignite | 2.18 |

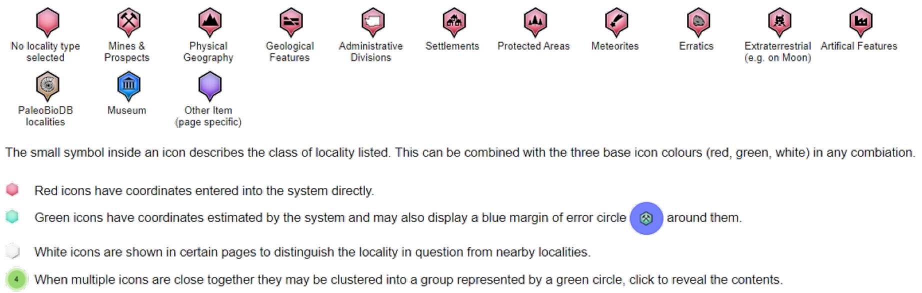


Davarpanah, E., Armandi, M., Hernández, S., Fino, D., Arletti, R., Bensaid, S., & Piumetti, M. (2020). $CO_2$ capture on natural zeolite clinoptilolite: Effect of temperature and role of the adsorption sites. *Journal of environmental management*, *275*, 111229.
Dosa, M.; Grifasi, N.; Galletti, C.; Fino, D.; Piumetti, M. Natural Zeolite Clinoptilolite Application in Wastewater Treatment: Methylene Blue, Zinc and Cadmium Abatement Tests and Kinetic Studies. *Materials* **2022**, *15*, 8191.

# ❑ CLINOPTILOLITE DEPOSITS and COMPOSITION




https://www.mindat.org/min-1082.html#autoanchor12




Clin has a different percentage of minerals comprising an amorphous phase, kaolinite, and illite, and the rest are Clinoptilolite minerals.

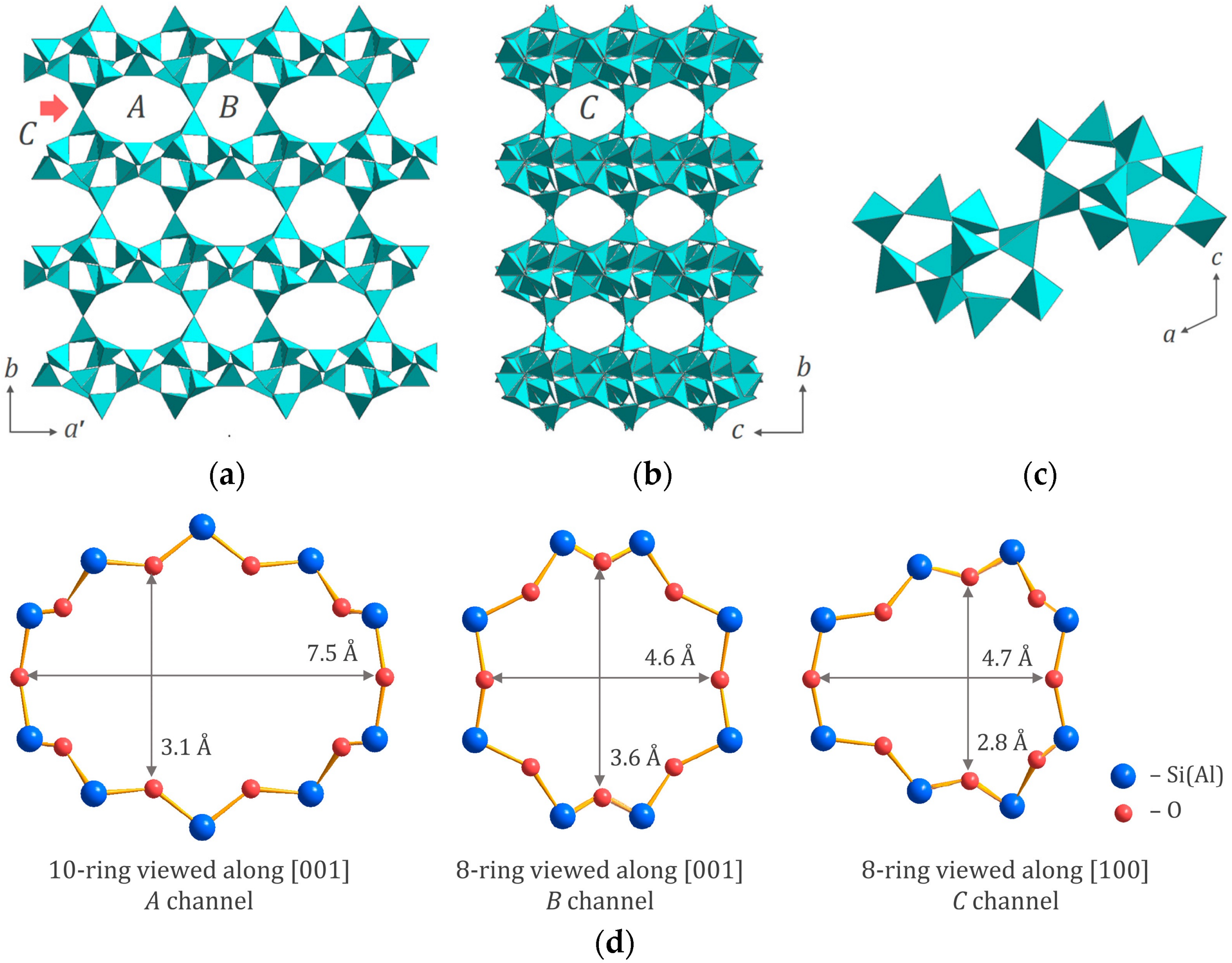
| Adsorbent material: Clin | | |
|---|---|---|
| QPA results (wt.%) | Clinoptilolite | 66.4 (1) |
| | Illite | 0.8 (2) |
| | Kaolinite | 4.0 (2) |
| | Amorphous phase | 28.8 (1) |
| Refinement statistic | $R_{wp}$ (%) | 0.089 |
| | Rp (%) | 0.059 |
| | $RF^2$ (%) | 0.086 |

The clinoptilolite framework is occupied by a variety of exchangeable cations (Ca2+, Na+ , K+, and Mg2+) with water bound in the cavities in the hydrated form.

Chemical composition depends on the geographic area of mining.

Davarpanah, E., Armandi, M., Hernández, S., Fino, D., Arletti, R., Bensaid, S., & Piumetti, M. (2020). $CO_2$ capture on natural zeolite clinoptilolite: Effect of temperature and role of the adsorption sites. *Journal of environmental management*, *275*, 111229.
Dosa, M.; Grifasi, N.; Galletti, C.; Fino, D.; Piumetti, M. Natural Zeolite Clinoptilolite Application in Wastewater Treatment: Methylene Blue, Zinc and Cadmium Abatement Tests and Kinetic Studies. *Materials* **2022**, *15*, 8191.

# ❑ CLINOPTILOLITE FRAMEWORK




void volume about 34%, estimated from the water content. The water occupies micropores and channels, in which exchangeable cations take place: Na, K, Ca or others (Mg, Fe, Sr, Ba) depending on which geographical area the clinoptilolite comes from. The ratio Si/Al can vary from 4.0 to 5.3, according to the Lowenstein's rule: the ratio Si/Al is always larger than 1


Rodríguez-Iznaga, I.; Shelyapina, M.G.; Petranovskii, V. Ion Exchange in Natural Clinoptilolite: Aspects Related to Its Structure and Applications. *Minerals* **2022**, *12*, 1628.
Dosa, M., Piumetti, M., Davarpanah, E., Moncaglieri, G., Bensaid, S., Fino, D. (2021). Natural Zeolites as Sustainable Materials for Environmental Processes. In: Piumetti, M., Bensaid, S. (eds) Nanostructured Catalysts for Environmental Applications. Springer, Cham.

## ❑ DETAILES OF KINETIC MODEL PARAMETERS (I)

| | | | MB concentration (ppm) | | | |
|---|---|---|---|---|---|---|
| | | | Clin | | | AC |
| **Model** | **Equation** | **Parameters** | **100** | **200** | **250** | **250** |
| Pseudo First Order | 7 | $R^2$ | 0.2496 | 0.7594 | 0.9159 | 0.9188 |
| | | $k_1$ | 0.0116 | 0.0133 | 0.0111 | 0.0134 |
| | | $q_{e,fit}$ | 0.7371 | 6.3630 | 19.8459 | 51.4803 |
| | | $q_{e,exp}$ | 19.5897 | 41.4197 | 56.2159 | 53.5020 |
| Pseudo Second Order | 8 | $R^2$ | **1** | **1** | **0.9985** | **0.9786** |
| | | $k_2$ | 0.4460 | 0.0127 | 0.0033 | 0.0005 |
| | | $q_{e,fit}$ | 19.4932 | 41.4938 | 55.5556 | 56.8182 |
| | | $q_{e,exp}$ | 19.5897 | 41.4197 | 56.2159 | 53.5020 |
| Intraparticle Diffusion | 4 | $R^2$ | 0.3017 | 0.4887 | 0.6499 | 0.9707 |
| | | $k_i$ | 0.5235 | 1.1673 | 1.9014 | 3.1658 |
| | | $C$ | 13.7420 | 25.6400 | 28.5310 | 3.9967 |
| Elovich | 9 | $R^2$ | 0.4478 | 0.7116 | 0.8158 | 0.9613 |
| | | $\alpha$ | 1693.8155 | 360.2312 | 175.6284 | 6.4746 |
| | | $\beta$ | 0.5850 | 0.2275 | 0.1559 | 0.1067 |
| Bangham | 5 | $R^2$ | 0.3179 | 0.3889 | 0.4279 | 0.9158 |
| | | $\vartheta$ | 0.2147 | 0.2704 | 0.3063 | 0.5562 |
| | | $k_B$ | 7.4536 | 11.2211 | 12.1399 | 2.8460 |
| Avrami | 10 | $R^2$ | 0.3992 | 0.7133 | 0.7088 | 0.6826 |
| | | $n$ | 0.2150 | 0.2959 | 0.2404 | 0.4954 |
| | | $k_A$ | 1.7049 | 0.8992 | 0.7728 | 0.1353 |

$$q = \frac{(C_0 - C) \cdot V}{m}$$



Dosa, M.; Grifasi, N.; Galletti, C.; Fino, D.; Piumetti, M. Natural Zeolite Clinoptilolite Application in Wastewater Treatment: Methylene Blue, Zinc and Cadmium Abatement Tests and Kinetic Studies. *Materials* **2022**, *15*, 8191.

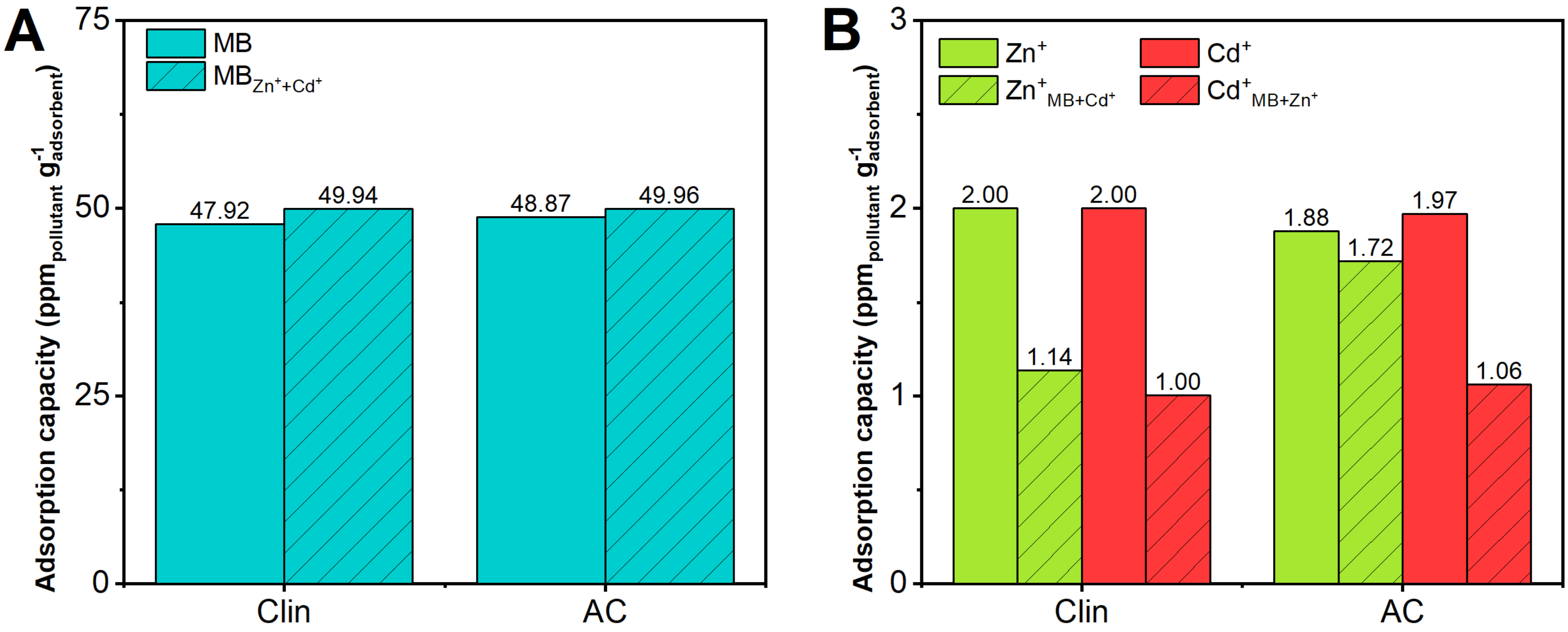
## ❑ DETAILES OF KINETIC MODEL PARAMETERS (II)

| | | | $C_{MB}$ =250 ppm; $C_{Zn}$ =10 ppm; $C_{Cd}$=10 ppm | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | Clin | | | AC | |
| **Model** | **Equation** | **Parameters** | **MB** | **Zn** | **Cd** | **MB** | **Zn** | **Cd** |
| Pseudo-First-Order | (7) | $R^2$ | 0.5591 | 0.2499 | 0.0434 | 0.7044 | 0.6648 | 0.1891 |
| | | $k_1$ | 0.0286 | 0.0167 | 0.0067 | 0.0650 | 0.0183 | 0.0086 |
| | | $q_{e,fit}$ | 2.0530 | 0.3422 | 0.0576 | 7.7145 | 1.7296 | 0.3836 |
| | | $q_{e,exp}$ | 22.2054 | 1.9820 | 0.643 | 24.4256 | 2.968 | 0.6300 |
| Pseudo-Second-Order | (8) | $R^2$ | 0.9999 | 0.9990 | 0.9995 | 0.9979 | 0.9902 | 0.9631 |
| | | $k_2$ | 0.0609 | 0.3228 | 1.8599 | 0.0108 | 0.0253 | 0.0699 |
| | | $q_{e,fit}$ | 22.2717 | 1.9716 | 0.6370 | 25.3807 | 3.1279 | 0.6797 |
| | | $q_{e,exp}$ | 22.2054 | 1.9820 | 0.6430 | 24.4256 | 2.968 | 0.6300 |
| Intraparticle Diffusion | (4) | $R^2$ | 0.3409 | 0.4493 | 0.3961 | 0.6889 | 0.9267 | 0.9844 |
| | | $k_i$ | 0.6897 | 0.0938 | 0.0289 | 1.7666 | 0.2322 | 0.0537 |
| | | $C$ | 15.1210 | 1.0874 | 0.3732 | 9.2597 | 0.5441 | 0.0353 |
| Elovich | (9) | $R^2$ | 0.4426 | 0.6557 | 0.6077 | 0.8979 | 0.9920 | 0.9616 |
| | | $\alpha$ | 1645.0404 | 3.6169 | 1.4994 | 10.1944 | 0.5882 | 0.0832 |
| | | $\beta$ | 0.5040 | 3.4758 | 11.0011 | 0.2013 | 1.6420 | 7.6746 |
| Bangham | (5) | $R^2$ | 0.3064 | 0.7467 | 0.2486 | 0.7299 | 0.9356 | 0.0402 |
| | | $\vartheta$ | 0.2317 | 0.1050 | −0.0474 | 0.5263 | 0.2646 | 0.0721 |
| | | $k_B$ | 2.0936 | 1.2354 | 0.7519 | 2.9032 | 0.8139 | 0.3194 |
| Avrami | (10) | $R^2$ | 0.4655 | 0.3438 | 0.2837 | 0.5768 | 0.5305 | 0.3941 |
| | | $n$ | 0.2664 | 0.2064 | 0.1804 | 0.5516 | 0.3342 | 0.2883 |
| | | $k_A$ | 1.4421 | 1.2376 | 1.4599 | 0.4703 | 0.4316 | 0.3639 |



Dosa, M.; Grifasi, N.; Galletti, C.; Fino, D.; Piumetti, M. Natural Zeolite Clinoptilolite Application in Wastewater Treatment: Methylene Blue, Zinc and Cadmium Abatement Tests and Kinetic Studies. *Materials* **2022**, *15*, 8191.

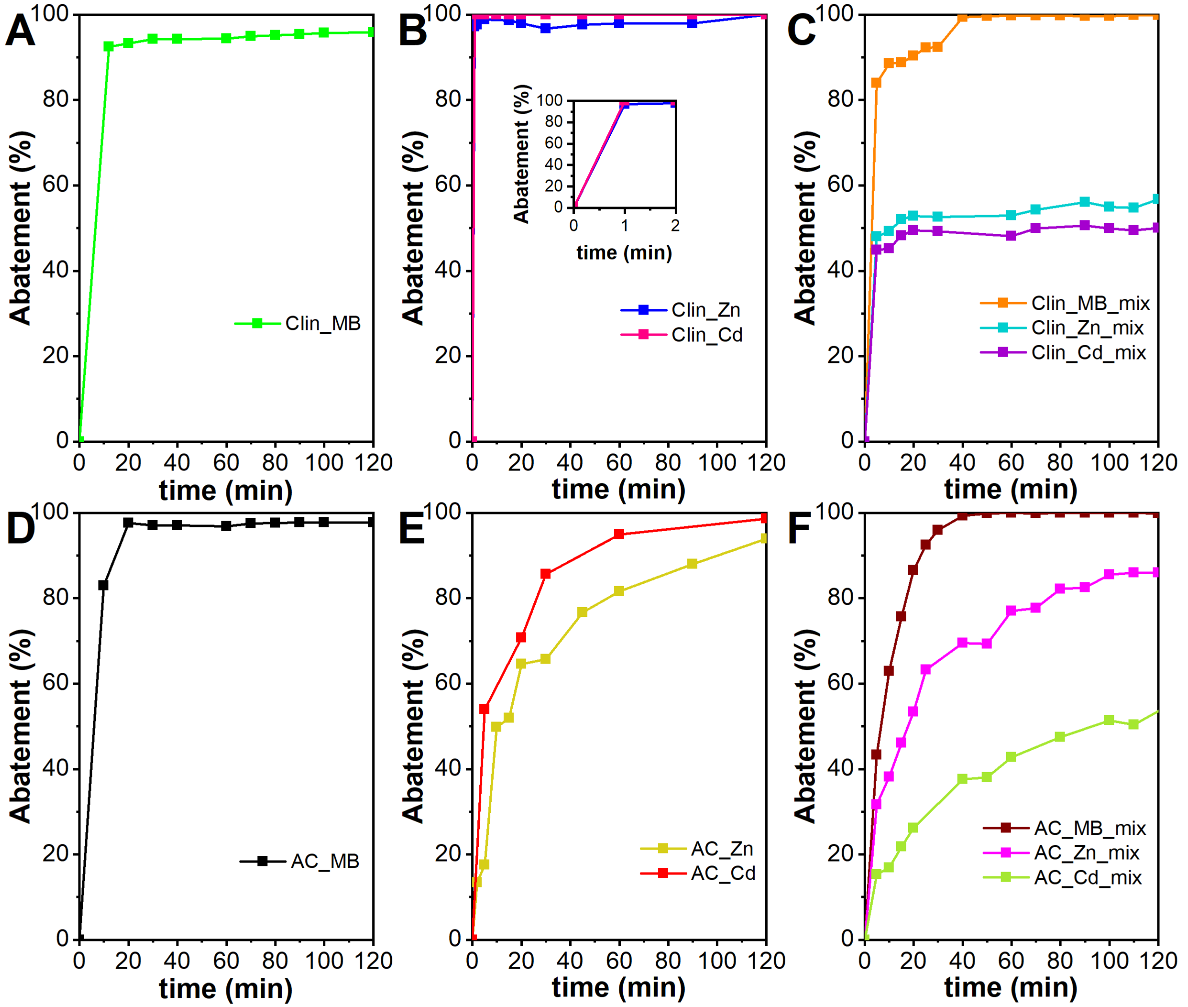
## ❑ ADSORPTION CAPACITY

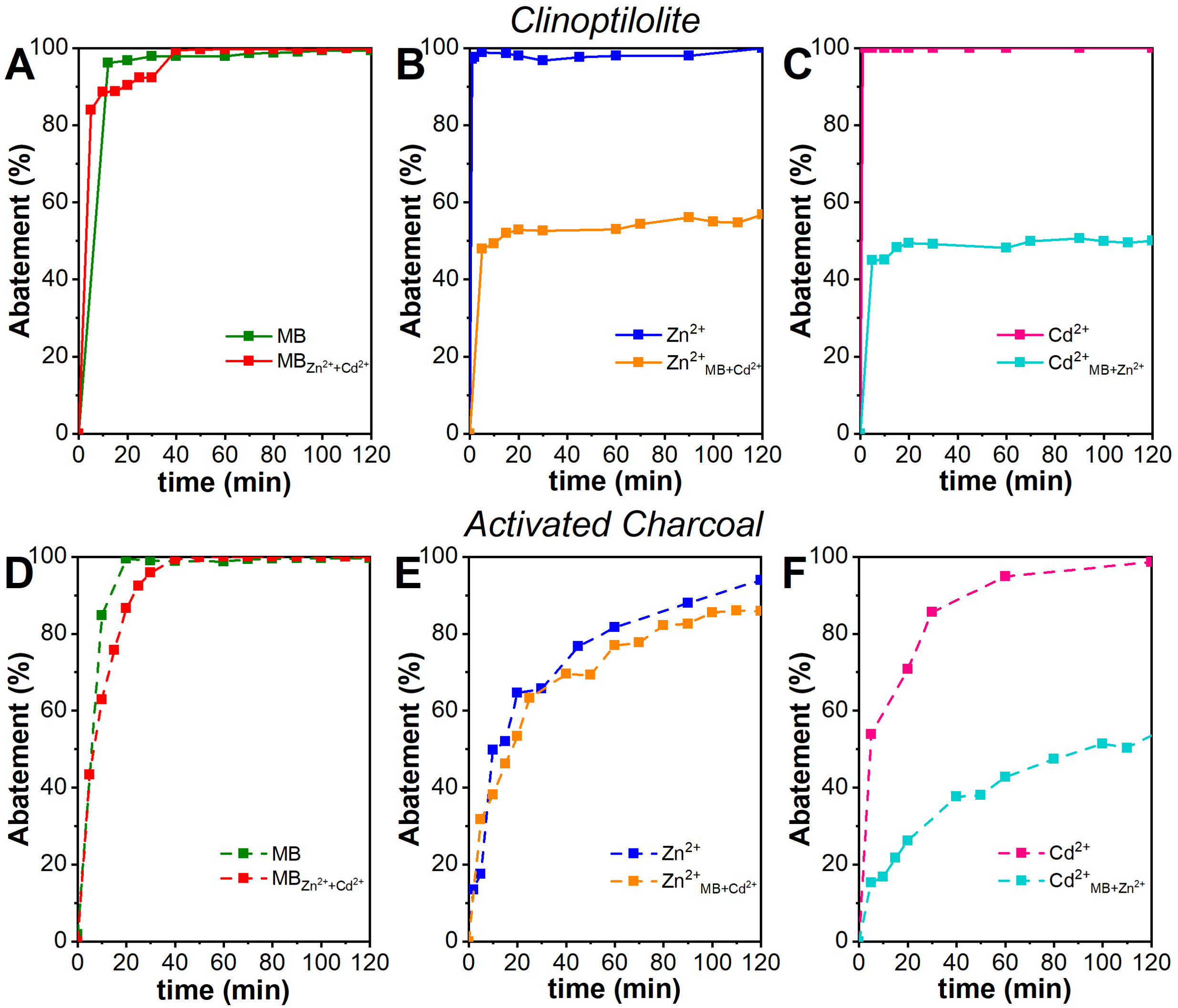





Dosa, M.; Grifasi, N.; Galletti, C.; Fino, D.; Piumetti, M. Natural Zeolite Clinoptilolite Application in Wastewater Treatment: Methylene Blue, Zinc and Cadmium Abatement Tests and Kinetic Studies. *Materials* **2022**, *15*, 8191.

# ❑ ABATEMENT DETAILS



| Adsorbent Material | MB Concentration (ppm) | pH $|_{time=0\ min}$ | pH $|_{time=210\ min}$ |
|---|---|---|---|
| Clin | 100 | 8.36 | 7.11 |
| | 200 | 8.01 | 5.65 |
| | 250 | 6.18 | 6.09 |

When the MB amount increases,
The pH decreases since the OH- species in solution are attracted to cationic MB, and the pH decreases to 8.01 and 6.18 at 200 and 250 ppm, time zero min, respectively.