

Natural zeolite clinoptilolite for wastewater treatment

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Introduction

The wastewater must be treated before the discharge to environment. Several pollutants and abatement techniques have been investigated by research studies. The organic compounds are usually produced from textile, paper and cosmetic industries (Adhikari, Palui, & Banerjee, 2009). The main issue of such pollutants is that they are stable to oxidation, light and heat (Adhikari et al., 2009). On the other hand, the metal cations are another class of contaminants in wastewater streams. Their maximum concentration in the lithosphere is regulated (Gazzetta Ufficiale della Repubblica Italiana, 2006).

Several abatement techniques were proposed for both organic compounds and metal cations and the most promising is the adsorption method. In this scenario, the zeolites could be interesting materials to be considered as adsorbent. The zeolites are microporous materials which have a three-dimensional structure. Moreover, they are able to have, inside their cavity, negative charge, due to the presence of $[AlO_4]^-$ (Dosa et al., 2018, 2021; Galletti, Dosa, Russo, & Fino, 2020). Thanks to this structural capability, the zeolites are able to be selective towards specific molecules. Among the zeolites, the natural ones can be considered due to their potential application and low cost comparing with the synthetic ones. The Clinoptilolite is a natural zeolite which could be used for the adsorption processes for wastewater treatment. This material exhibits good adsorption capacities towards organic and metal compounds, as evidenced by other research studies (Dosa et al., 2018, 2021; Galletti et al., 2020).

Experimental Methods

In this work, the Clinoptilolite was used for the adsorption of Methylene Blue ($C_{16}H_{18}ClN_3S$), Zn and Cd metal cations. The previous contaminants were chosen as probe pollutants. The Clinoptilolite was compared with Activated Carbon. The textural and structural properties of the samples were investigated by means of N_2 physisorption at 77 K and Field Emission Scanning Electron Microscopy (FESEM). The adsorption tests were performed with the following concentrations: 250 ppm of Methylene Blue, 10 ppm of Zn^{2+} , 10 ppm of Cd^{2+} and 5 g l^{-1} of adsorbent material.

The metal solutions are prepared from the nitrates as precursors. The adsorption tests are accomplished as the Methylene Blue ones. Finally, the Methylene Blue and metal cations adsorption capacities of Clinoptilolite and Activated Carbon are investigated. Also, for this study, the adsorption tests are performed as Methylene Blue ones. However, in this case, the collected suspension is analyzed via UV-Vis spectrometer and ICP-MS for Methylene Blue and metal cations concentrations, respectively.

Results and Discussion

In Table 1 are reported the textural properties as derived from the nitrogen physisorption analysis. The Clinoptilolite exhibits low SSA and pore volume comparing with the Activated Carbon. The morphology of the samples was investigated by means of FESEM micrographs and the results are reported in Figure 1. The Clinoptilolite has a flake-like structure while the Activated Carbon exhibits a multi-wallet mesoporous morphology.

Table 1. Textural properties of the materials obtained by N_2 physisorption at 77 K.

	N_2 physisorption at 77 K.	
	Specific Surface Area ($m^2\text{ g}^{-1}$)	Pore volume ($cm^3\text{ g}^{-1}$)
Activated Carbon	891	0.56
Clinoptilolite	32	0.12

In Figure 2A are reported the Methylene Blue adsorption capacities. As a whole, the Methylene Blue adsorption exhibits good performances for both Clinoptilolite and Activated Carbon. Interestingly, when the Methylene Blue is adsorbed with the copresence of metal ions, labelled as "Methylene Blue_Metals", the adsorption capacities are higher. Furthermore, the Clinoptilolite exhibits better adsorption performances

towards Zn and Cd (Figure 2B) comparing with Activated Carbon case study. The reason of such behavior is due to the ion-exchange process which occur during the abatement of metals: such pollutants are adsorbed on the Clinoptilolite better because the zeolite is rich in metal cations on its surface (Dosa et al., 2018, 2021; Galletti et al., 2020).

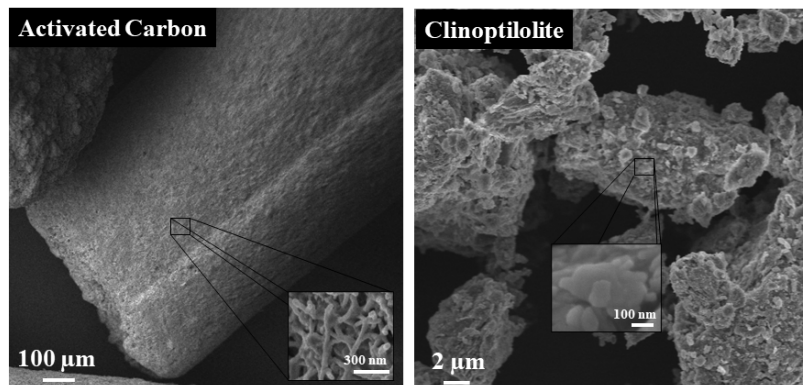


Figure 1. FESEM images of the adsorbent materials.

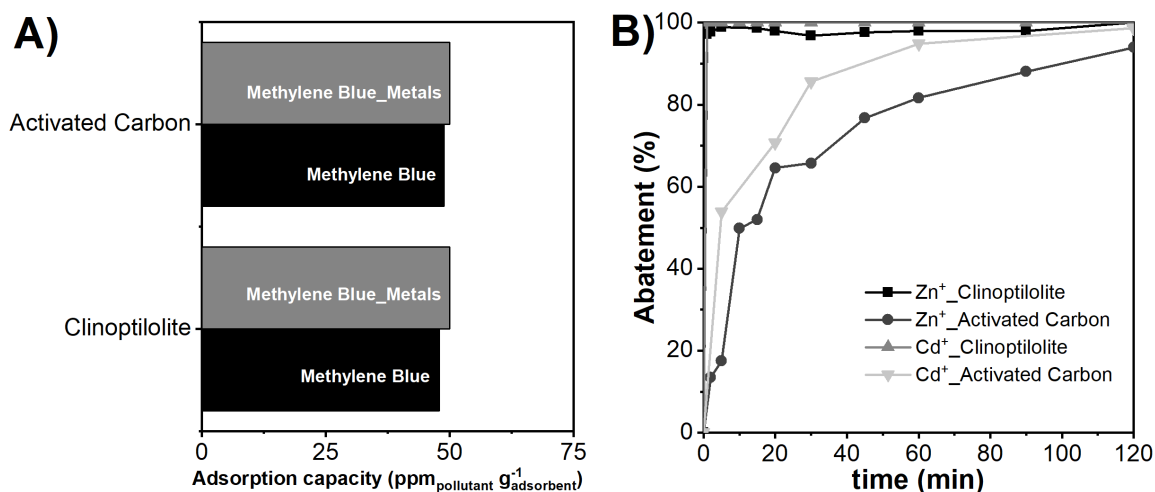


Figure 2. Adsorption capacities towards Methylene Blue and B) metals abatement over the time of Clinoptilolite and Activated Carbon

Conclusions

In conclusion, the Clinoptilolite, a natural zeolite, was used for adsorption tests towards Methylene Blue, Zn and Cd cations. The results have demonstrated the good adsorption capacities comparing with Activated Carbon, an adsorbent material which is commonly used for the adsorption abatement techniques. Thus, the Clinoptilolite could be used as valid alternative for adsorption technology in wastewater treatment.

References

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