The use of the clinoptilolite for wastewater remediation

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In nature there are more than 60 species of zeolite (namely, volcanic and sedimentary rocks) from which many of them are in the sedimentary deposits. The zeolites that occur more frequently are the following: clinoptilolite, mordenite, chabazite, analcime, phillipsite, erionite and heulandite. Among them, the clinoptilolite is probably the most studied material for the adsorption of either organic molecules or metal ions in the wastewater treatment. Likewise, it has been used for the treatment of nuclear wastewaters and in the agriculture field as a slow-release nitrogen fertilizer.

The general formula of the clinoptilolite is $(NaKCa)_4(Al_6Si_{30}O_{72})\cdot 24H_2O$ along with other cations (e.g. Fe, Mg). The textural properties of this material are very interesting for the hazardous waste management: it has a void volume of about 34% and it is characterized by the co-presence of multi-porosities: micro- (< 2 nm), meso- (between 2 and 50 nm) and macro-porosity (> 50 nm). Moreover, the cation exchange capacity is ca. 2.25 m_{equiv} g^{-1} and the affinity with cations follows the order: Li < Mg < Al < Fe < Ca < Na < Sr < Ba < NH_4 < K < Rb < Cs.

In the present work, the clinoptilolite was used for the adsorption of both organic compounds (methylene blue and Acid Orange AO7 as probe molecules) and metal ions (Zn, Cd). Moreover, the degradation of Acid Orange 7 (AO7) via a Fenton-type process was investigated using a 10 wt.% Fe-clinoptilolite sample prepared by the ion-exchange procedure. Then, complementary techniques were used to characterized the physico-chemical properties of the zeolite (Dosa et al. 2018).

As a whole, the specific surface area of the powder clinoptlilolite is lower (42 m^2 g^{-1}) than that of ordered micro- and mesoporous materials (typically above 100 m^2g^{-1}). Moreover, the Fe-clinoptilolite sample exhibits a partial reduction of the BET surface area (33 m^2g^{-1}) as compared to pure clinoptilolite. The average pore size is 15 nm evaluated by the BJH method.

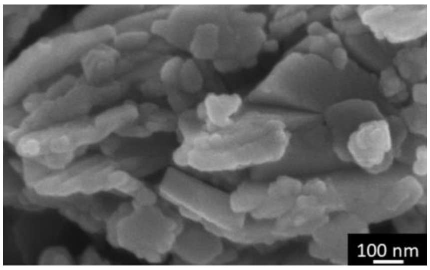

Figure 1. FESEM image of the clinoptilolite.

The morphology of the clinoptilolite was assessed by the FESEM analysis (Figure 1): it seems to have anhedral particles (lamellar structures) assembled on the top of each other. This shape is the result of a self-assembly during the initial phases of clinoptilolite that does not crystallize. In fact, the crystal growth began in an environment with no free space for the formation of these crystal facets. The chemical analysis of the clinoptilolite revealed the presence of Fe (0.68 wt.%) and Mg (0.47 wt.%) as impurities, whereas 7.2 wt.% of Fe was detected on the Fe-clinoptilolite sample.

In order to evaluate the adsorption capacity of the clinoptilolite towards organic compounds, several adsorption tests were performed with solutions of MB and A07 (250 and 500 mg l^{-1}). Concerning the MB adsorption, the results have shown that the abatement is more efficient in the case of 250 mg L^{-1}, about 96 % after 2h. For the solution 500 mg L^{-1} the abatement is about 93% after 2h. The kinetic order of MB adsorption has been evaluated. The results suggest a second order reaction (Figure 2). On the other hand, the A07 adsorption was not observed after 2 hours (even if at different pH values) probably due to the presence of electrostatic forces Na^+ SO_3^--[…] into the molecular structure.

Nevertheless, the degradation of AO7 (500 mg l^{-1}) over the Fe-clinoptilolite was proved. In particular, the Fenton-type reaction was particularly effective in the presence of both H_2O_2 and ascorbic acid as oxidant and reductant reagents, respectively. Specifically, ca. 60% AO7 conversion was achieved over the Fe-clinoptilolite when H_2O_2 was added to the solution containing the ascorbic acid. On the other hand, much lower conversion values were achieved in the absence of the H_2O_2/ascorbic acid, in agreement with previous studies (Piumetti, Freyria *et al.*, 2014, 2016, 2017). These results confirm the important role (= synergistic effect) of both oxidant and reductant agents in Fenton-like processes under dark condition.

Finally, the adsorption capacity of the clinoptilolite was tested for an aqueous solution with metal ions (Zn, Cd, 200 mg l^{-1}). Interestingly, more than 98 wt.% of metals was adsorbed in 3 hours, thus showing better adsorption capacity than the active carbon. All these results confirm the key role of the clinoptilolite in the waste water remediation.

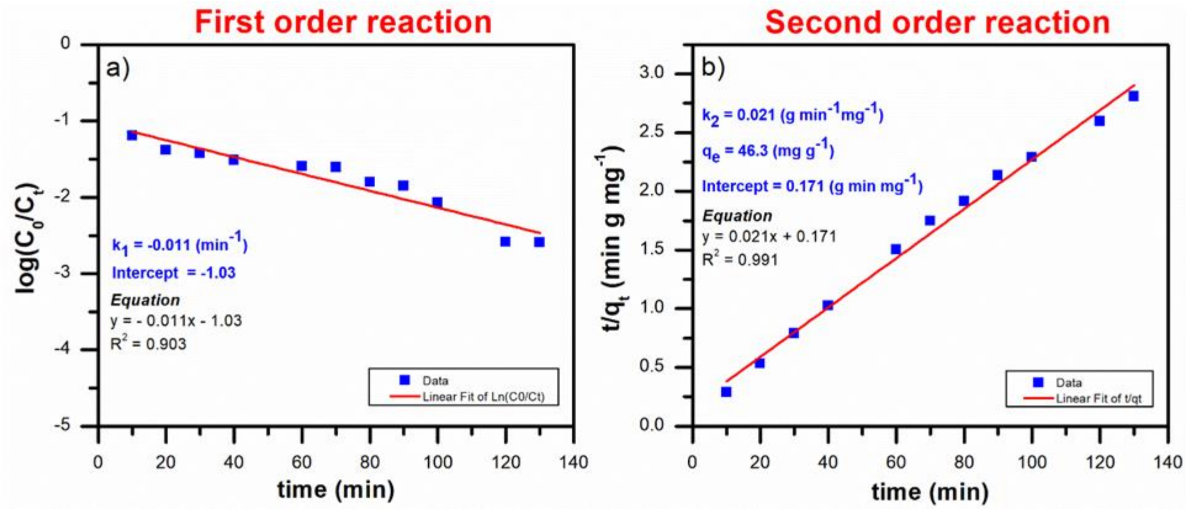

Figure 2. The adsorption of MB (500 mg l^{-1}) in the case of a first order reaction a) and the second order reaction b).

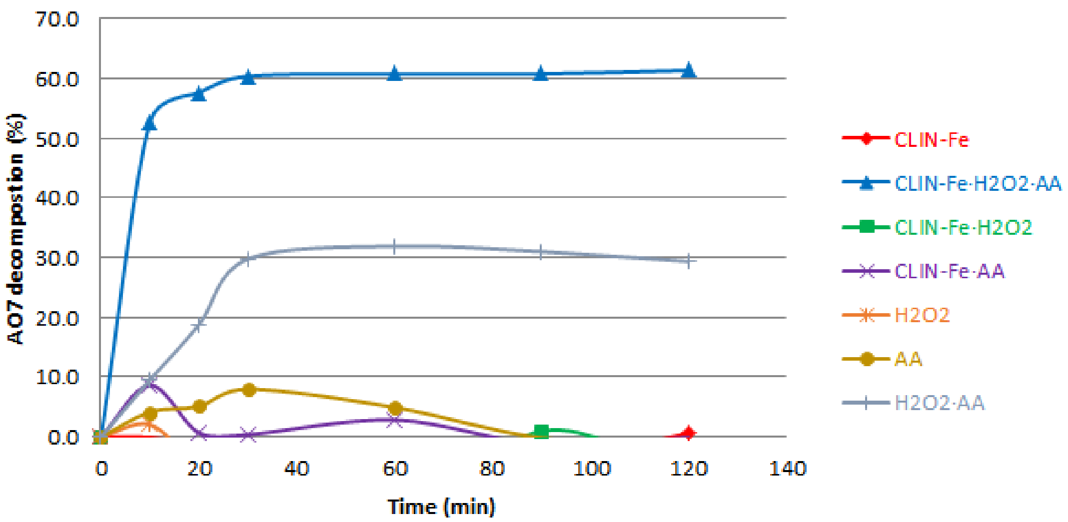

Figure 3. AO7 decomposition (%) over the time (min.) using different operating conditions. The AO7 decomposition takes place via a Fenton-type mechanism.

Reference

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