

## Editorial

# Special Issue “Sustainable Remediation Processes Based on Zeolites”

Claudia Belviso 

National Research Council, Institute of Methodologies for Environmental Analysis—CNR-IMAA,  
Contrada S. Loja—Zona Industriale, 85050 Tito Scalo, Italy; claudia.belviso@imaa.cnr.it

Zeolites are microporous tectosilicates characterized by a three-dimensional network of tetrahedral (Si, Al)O<sub>4</sub> units with the general formula:  $Mx^+Ly^{2+}[Al_{(x+2y)}Si_{1-(x+2y)}O_{2n}]\cdot mH_2O$  where M<sup>+</sup> and L<sup>2+</sup> are monovalent and divalent cations [1]. Due to this structure, zeolites show specific and interesting properties such as large surface areas and a high cation exchange capacity making these minerals very useful in many contexts. Therefore, because of these numerous applications, the demand for zeolites has greatly increased and this is documented by an annual production/consumption of both natural and synthetic zeolite which already in 2016 stood at ~2.8 million and ~1.6 million tons, respectively [2]. The most common natural zeolites are clinoptilolite-heulandite, mordenite, phillipsite, chabazite, analcime and numerous deposits of these minerals are distributed throughout the world. The application of natural zeolites for environmental purposes is becoming important also thanks to their low cost and the ease of finding them. Regarding synthetic zeolites, in the last few years, great attention has focused on defining new raw materials to be used as a source, including wastes [3–5] and in setting up different processes for their formation [6]. Moreover, much data have paid great attention to synthetic zeolites in the environmental remediation field.

Unfortunately, environmental pollution represents one of the greatest problems that afflicts humanity and for which humans themselves are responsible. Domestic and municipal wastes, industrial, military and agriculture activities, mining and petrol-derived products represent the main anthropogenic sources of soil and water pollution. They are responsible for contamination by both inorganic and organic pollutants. Along with the other inorganic contaminants, metals represent the main source of pollution. Although these elements naturally occur at low concentrations in soils and sometimes represent useful micronutrients for plants, when present in high amounts due to anthropogenic activities, have toxic effects because these elements are generally not degradable. Persistent and mobile organic compounds (PMOCs) and organic dyes are instead the most diffuse organic pollutants. PMOCs are emerging contaminants which are released from many sources and despite the low concentrations (from ng to a few  $\mu\text{g L}^{-1}$ ) they are significant as they are toxic. Among these, antibiotics are of particular concern due to their prevalence in human as well as veterinary medicine and, as consequence, their large concentration in wastewater.

Several environmental remediation technologies based on zeolites have been developed to clean up contaminated water [7–9], whereas the literature data on the use of these natural and synthetic minerals for polluted soil remediation are yet significantly lower [10].

This Special Issue of *Processes* on “Sustainable Remediation Processes Based on Zeolites” collects recent papers describing advances in remediation technologies based on these very useful minerals. The issue includes a review paper providing a summary of studies concerning the use of zeolites in soil remediation and discussing the limitations on zeolite applications [11]. Many studies have described the ability of zeolite in restraining Pb uptake by plants, alleviating metal-toxicity (Cd, Ni, and Zn) stress or improving soil fertility. However, there is limited information in the literature about the potential



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disadvantages of the long-term application especially of natural zeolites while the general stability especially of added synthetic zeolites in soils is still a matter of concern.

The other works analyze the successful use of these natural and synthetic microporous/mesoporous materials to reduce toxic metals and organic contaminants from water [12–18]. For instance, Mancinelli et al. [12] studied the efficiency of 13X and ZSM-5 synthetic zeolites in heavy metals and volatile organic compounds (VOC) removal from polluted water of an industrial area designated as Contaminated Sites of National Interest. The study was performed at a pilot scale and under real environmental conditions, providing a rapid and low-cost solution for the decontamination. In detail, ZSM-5 zeolite showed high removal efficiencies (>87%) in volatile organic compounds (in particular 1,2-dichloroethylene and trichloroethylene), whereas 13X zeolite permitted heavy metals abatement up to 100%. Ugrina and co-workers [13], instead, used natural zeolite (clinoptilolite) chemically modified with Na<sub>2</sub>S at 150 °C to remove Hg(II) from polluted aqueous solutions. According to the authors, the toxic element removal by clinoptilolite impregnated with sulfur species (FeS and CaS) took place by several mechanisms including ion exchange, surface complexation, electrostatic attraction and co-precipitation of the Hg in the form of HgS. The sorption capacity of modified clinoptilolite was also compared with that of not modified natural zeolite showing an increase of 3.6 times its efficiency in toxic element remediation (from 0.28 mmol/g to 1.02 mmol/g). Furthermore, the paper by Kuntubek and co-workers [14] describes the application of clinoptilolite for water remediation and in particular the authors studied the ability of three samples of clinoptilolite-based silver and magnetic nanocomposite for methylene blue (MB) remediation. Natural zeolite was impregnated with silver nanoparticles (20 nm in size) or silver oxides (42 nm in size) or magnetite (32 nm in size) and added to the polluted solution. The results indicated that physical adsorption determines MB removal by 25–36%. Moreover, the sample of clinoptilolite with Fe<sub>3</sub>O<sub>4</sub> was more effective in remediation leading to 55% and 97% of contaminant removal without oxidant or in the presence of H<sub>2</sub>O<sub>2</sub>, respectively. Clinoptilolite, together with a clay mineral (montmorillonite) and with a sample of biochar, was also used as an adsorbent to remove 226Ra from an aqueous solution and groundwater during the tests described by Almasoud et al. [15]. Radium is naturally present in large amounts in water and groundwater mainly due to the interaction with a specific type of bedrock such as igneous rocks. However, humans contribute to this toxic element pollution with activities dealing with oil and gas production or with the extensive use of phosphate fertilizers in agriculture. The results of this work display that zeolite can be successfully used for 226Ra remediation and it has a higher removal efficiency reducing the concentrations of the toxic element in all analyzed groundwater samples to less than permissible concentrations for drinking water (0.5 Bq L<sup>−1</sup>). The authors describe the mechanism of 226Ra adsorption by zeolite (as well as for the other materials investigated) as a combination of processes including sorption, and/or external mass transfer and intraparticle diffusion through the macropores and micropores. The adsorption mechanism is well shown by Freundlich and Temkin's models. Boycheva and co-workers [16] used Na-X type zeolite formed from a waste material (lignite coal fly ash) as well as their modified structures (with magnetic nanoparticles or loaded with cobalt and copper oxides) to remove Cd<sup>2+</sup> and Pb<sup>2+</sup>-ions from aqueous solutions. The modified zeolites were also tested as catalysts for thermal Fenton oxidation of methylene blue. All the samples show high efficiency toward the removal of Cd<sup>2+</sup> and Pb<sup>2+</sup>-ions from aqueous. The results indicate that all zeolites adsorb Pb<sup>2+</sup> ions up to concentrations of 100 mg/L and were effective in cadmium ion removal up to concentration levels of 50 mg/L. At higher concentrations of Cd<sup>2+</sup>-ions, stronger adsorption was observed by zeolite sample modified with maghemite nanoparticles. All the samples also reveal high catalytic activity in a Fenton oxidation process of methylene blue although metal oxide modified zeolites are preferable. Finally, Ellersdorfer and co-workers [17] studied the action of ion-exchanger-loop-stripping process based on zeolite for nitrogen recovery from swine manure. The experiments were performed at a pilot

scale using natural zeolite from Slovenia mainly represented by clinoptilolite. The results indicate that ammonium removal rates of 85 to 96% were achieved.

The above papers demonstrate the interest in developing new technologies for water and soil remediation based on the use of zeolites. With the enormous variety of environmental problems and the increasing waste production, I feel confident for the future of zeolite in the field of remediation technologies, also coupled with the development of processes based precisely on the use of wastes for zeolite synthesis. The use of zeolite formed from wastes to solve environmental pollution is perfectly in accordance with the concept of the circular economy, of great relevance and topicality.

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