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# Application of natural zeolites in environmental remediation: A short review ☆

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ABSTRACT

The natural zeolites have already found extensive applications to the environmental remediation and restoration. The most of these applications are based on their ion-exchange properties. This contribution provides a short review of the recent literature concerning the utilization of natural zeolites and their modified forms in the separation, binding and chemical stabilization of hazardous inorganic, organic and radioactive species in soils and aqueous systems. The advantages and eventual disadvantages of the techniques are also discussed.



## 1. Introduction

The population growth in the urban areas, the oil and goods transportation, the emissions from vehicle exhausts, the mining and smelting activities, the energy production, and the, frequently uncontrolled, use of pesticides resulted in the accumulation of huge amounts of hazardous inorganic and organic pollutants in the environment. Severe environmental contamination has also been observed in cases nuclear reactors accidents, explosions in nuclear waste storage facilities and in the surroundings of a number of military and civil fuel reprocessing plants around the world.

When the concentration of the pollutants exceeds certain limits and their presence seriously endangers the environment and the human health, remediation actions are necessary. The remediation can mainly be based on two approaches: the extraction of the pollutants from the soils or aqueous systems or the reduction of their mobility and/or their *in situ* stabilization [1,2].

Although a number of materials and techniques have been utilized for these purposes, the use of natural zeolites and their modified forms offer as advantages the low-cost, the availability in big quantities in many (even economically weak) parts of the world, the good mechanical and thermal properties and the combination of high sorption capacity with the ability to modestly adjust the pH of the soil or the aqueous system. In addition, the natural zeolites, do not introduce additional pollution in the environment.

This contribution will provide an short review of the most recent applications of natural zeolites and their modified forms to the separation, binding and chemical stabilization of hazardous inorganic, organic and radioactive species in soils and aqueous systems, the treatment of acid mine, industrial and municipal effluents and the pedotechnical restoration.

## 2. Natural zeolitic materials and environmental remediation

The application of natural zeolites to the environmental remediation is mainly based on their ion-exchange properties [3]. It is also well-known that ion-exchange in the case of zeolites takes place among cations and only their modification can provide them with anion sorption properties.

The uptake of metal cations from solutions by the zeolites is affected by a variety of factors such as the temperature, the solution pH, the presence of competing cations and complexing agents, the dimensions of the hydrated dissolved species compared to the opening of their channels and the external surface activity [4].

Experiments but also thermodynamic investigations have indicated an enhanced selectivity of the zeolites towards monovalent ions and especially $Cs^+$ and $NH_4^+$. The selectivity towards bivalent cations (e.g. $Sr^{2+}$, $Pb^{2+}$) is much lower (e.g. [5–8]. Multicomponent sorption experiments and thermodynamic calculations were also performed in several cases (e.g. [9,10]. However, the thermodynamic calculations in the case of natural zeolitic materials are not always simple because of their composition complexity (e.g. presence of other sorbing phases, varying zeolite content, etc.).

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The uptake of transition elements and actinides by natural zeolites strongly depends on their aqueous chemistry and their hydrolysis reactions yielding a variety of soluble or insoluble products which interact with the zeolite. In these cases the uptake mechanisms do not solely comprise absorption/ion-exchange and adsorption but also surface precipitation/coprecipitation [11–14].

The application of natural zeolites to the environmental remediation is not new (e.g. [15] and a number of articles and books have appeared on this subject (e.g. [16–19]. However, the intense investigation of the natural zeolites properties started in the middle of the previous century, when materials with enhanced sorption capacity were necessary for the nuclear waste management (e.g. [20]. A number of patents on the application of clinoptilolite to the immobilization of radioactive cesium isotopes already appeared around 1960 (e.g. [21] and the interest in this field is still actual (e.g. [22]. Natural zeolites were used for the limitation of the consequences of the Three Miles Island and Chernobyl nuclear accidents [23–25], for the removal of radioactive Cs- and Sr-isotopes from nuclear industry effluents [26] and for the decontamination of waters. It is worth mentioning that the use of natural zeolite (clinoptilolite) in the Sellafield Ion Exchange Effluent Plant (SIXEP), in operation since 1985, reduced the $^{137}Cs$ and $^{90}Sr$ discharges to the Irish Sea to relatively constant low levels considerably improving the radiological conditions of this highly polluted area [27]. Regions rich in natural zeolites (e.g. Yucca Mountains, Nevada, USA) were also proposed as potential nuclear waste repositories [28].

The removal of heavy metals (e.g. Fe, Pb, Cd, Zn) from acid mine drainage is another field of potential environmental applications of natural zeolitic materials [29–32]. The regeneration of the zeolites by a number of solutions was also investigated in some cases. In the case of Zn the following rank of desorption effectiveness was observed EDTA > NaCl > $NaNO_3$ > NaOAc > $NaHCO_3$ > $Na_2CO_3$ > NaOH > $Ca(OH)_2$. For cyclic Zn absorption/desorption, the adsorption remained satisfactory for six to nine regenerations with EDTA and NaCl, respectively [33].

The removal or stabilization of heavy metals, and especially lead, in environmental matrices was the object of a number of investigations that recently appeared in the literature. Phillipsite and faujasite were successfully used to stabilize lead, cadmium and nickel in contaminated soils [34]. The mixed treatment (zeolite and humic acids) of artificially Pb-polluted garden soil resulted in significantly greater reduction in the lead concentration in plants compared to the addition of single zeolite but slightly increased the water-soluble fraction of lead compounds in the soil [35].

Laboratory-scale investigations and field tests indicated the effectiveness of natural zeolites and their modified forms to reduce the concentration of heavy metals and hazardous substances in plants and their ecological significance in revegetating land affected and made barren by metal pollution. This also has as consequence the limitation of the ground erosion [36].

Clinoptilolite was studied as sorbent of lithium for the protection of poplar plants grown in the contaminated soil. Lithium was selected as a model contaminant as it could be tracked directly using nuclear magnetic resonance [37]. Studies utilizing Neapolitan Yellow Tuff (NYT) in abating soil Cu-, Pb- and Zn-toxicity against living organisms also showed that the presence of the zeolites restored a friendly to biota soil environment, by leading to a substantial recovery of the fertilization success and of the vitality, with a concurrent significant reduction of pathologies and mortality ([38]). On the other hand, NYT was also utilized as a component of an organo-mineral sorbent/exchanger soil conditioner with pellet manure to reduce the mobility of Cd and Pb and recover plant performance in heavily polluted soils from illegal dumps in Campania, Southern Italy [39].

The pedotechnical applications of natural zeolites/organic matter mixtures and their synergy to phytoremediation are a subject of continuous intensive investigation and will gain further importance in the future [36]. However, there is only limited information in the literature about the potential disadvantages of the long-term application of natural zeolites. Their influence on the soil pH and essential metal availability, the possibility to release considerable amounts of sodium and the long-term binding of polluting metals in the soil were just a few of the problems pointed out [40].

The purification of waters and the treatment of industrial and urban wastewaters are further fields of applications of natural zeolitic materials [4,25,41–50]. Natural zeolites were mainly investigated and applied as sorbents for ammonium from urban as well as for heavy metals and dyes from industrial wastewaters. Wastewater treating facilities utilizing natural zeolites are already in operation in many countries. The removal of nutrients species (e.g. $NH_4^+$, $H_2PO_4^{2-}/HPO_4^-$), quantitative precipitation and recovery in the slow release fertilizer was also reported in the literature [51].

The application of natural zeolitic materials to the reduction of heavy metals and petroleum products in motorway stormwaters was also considered [52]. Especially, the effectiveness of a combined use of materials (zeolite + lava and limestone, zeolite + vermiculite) was investigated [53,54].

The potential utilization of natural zeolites for treating saline/sodic coal bed natural gas (CBNG) produced waters was investigated and presented in the literature. For this purpose Ca-rich clinoptilolite were examined as potential sodium sorbents from CBNG waters. Column tests indicated that a metric tonne (1000 kg) of St. Cloud- and Brazilian-zeolite could be used to treat 16,000 and 60,000 L of CBNG water, respectively, in order to lower its sodium adsorption ratio (SAR, mmol½ L-½) from 30 mmol½ L-½ to an acceptable level of 10 mmol½ L-½ [55,56]. The reduction of sodium in seawater by natural zeolite and chlorine by calcined hydrotalcite was also attempted for agricultural applications [57].

Finally, ferritized and mechanically activated natural zeolitic materials were also investigated as potential materials for specific environmental applications [58–60].

## 3. The application of surfactant- modified zeolites to the environmental remediation

An especially interesting class of materials for the environmental remediation is the surfactant- modified zeolites. These materials, which combine the enhanced cation sorption properties of natural zeolites with the ability to sorb anionic species, non-polar organic species and pathogens from aqueous streams, are considered for applications as decontamination agents for soils and water basins, backfill and sealing materials in waste repositories and as permeable reactive barriers for the cleaning of waters [61]. The most frequently modifying agents are quaternary amines (e.g. HDTMA, ODTMA, *N*-cetylpyridinium), which form on the zeolite surface a bilayer-like structure altering its surface charge (from negative to positive). The positive surface charge provides sites for sorption of anions, whereas the organic-rich surface layer provides a partitioning medium for sorption of non-polar organic compounds. The zeolite's original cation exchange capacity is also partly retained.

Investigations have shown that natural zeolites modified by surfactants can successfully bind anionic species of metals (e.g. arsenates, chromates, iodides, nitrates, perchlorates, antimonates) (e.g. [62–67]. Similar sorption properties and capacity show the polymer-modified zeolites (e.g. by polyhexamethylene-guanidine) [68–70]. The preparation of pellets of surfactant-modified mixed with zero-valent iron provides the possibility of contaminants removal by combined reduction/sorption action [71,72].

The surfactant-modified natural zeolites were found to be effective in the treatment of oilfield wastewaters and sorption of volatile petroleum hydrocarbons (e.g. BTEX: benzene, toluene, ethylbenzene and xylenes) [73–76]. The column regeneration by air sparging was also investigated [77].

The zeolite particles are good carriers of bacteria, which increase the sludge activity in wastewater treatment plants. A significant drawback of this application is the slow formation of the bacteria layer on the zeolite surface, which does not become immediately effective (it takes almost a week). The modification of zeolites by cation active polyelectrolytes accelerates the interaction among the bacteria with the zeolite surface further increasing the sludge activity [78]. The surfactant-modified zeolites also show the ability to bind pathogens (e.g. *Escherichia Coli*) from sewage [61,79,80].

## 4. The use of natural zeolites in permeable reactive barriers

The leakage of municipal, industrial and radioactive waste disposal sites frequently results in distribution of contaminants in cationic, anionic or non-polar form in the surrounding environment. These sites require limitation by materials that retain the contaminants (e.g. radionuclides, health endangering metals, organic compounds) but allow the passage of groundwater. Sorbent and/or reactive materials emplaced in permeable subsurface barriers are promising tools for dealing with the groundwater contamination problems. [81–89]. The high sorption capacity, plasticity, chemical stability, mechanical strength, thermal conductivity made the raw and modified natural zeolitic materials, along with the clays, suitable for utilization as liners prohibiting the spreading of the contaminants. The use of surfactant-modified zeolite as a permeable barrier sorbent may offer several unique advantages when dealing with mixed contaminant plumes [90,91]. The *in situ* microbial regeneration of permeable reactive of barriers was also investigated (e.g. [78,92]. This technique can lead to sustainable use of the sorption materials avoiding frequent replacement or external regeneration

Especially interesting is also the application of permeable barriers combing the sorption with chemical reduction by zero valent iron or the biological degradation of the contaminants by microorganisms [61,93]. In the case of biodegradation specialized microorganisms can be cultured on the surfactant-modified zeolite. The nutrients (e.g. potassium and ammonium), required for the microbial metabolism, can be preloaded onto the zeolite.

Finally, the application of clinoptilolite in permeable barriers for the treatment of heavy metal contaminated waters in Antarctic was also considered. However, it should be mentioned that the fixed-bed performance of the zeolite was found to be significantly reduced at low temperatures. As indicated in the literature the breakthrough points and saturation capacities observed at 2 °C are 60–65% lower than those at 22 °C [94]. Clinoptilolite was also found to exhibit a significant interaction between moisture and freeze–thaw with a coarsening of the mean grain size in the presence of water and cracks forming fragments appearing in the zeolite grains. These findings may have implications for the long-term permeability of the reactive barriers operated in areas of freezing ground [95].

## 5. Conclusions

The sorption capacity of the raw- and modified natural zeolites cannot be compared with this of the synthetic materials possessing tailored composition, structure and properties. However, this drawback can be compensated by the low-cost of natural zeolitic materials and their availability in big quantities in many parts of the world.

One should also mention that there are still immediate challenges for further successful environmental applications of this interesting class of natural materials. A variety of novel soil and water/wastewater treatment technologies can be developed on their basis. The improvement of the long-term chemical and physical stability of the modified zeolitic materials and the combination of their sorption properties with the contaminant destruction can also be subject of further academic and industrial research. Finally, the consideration of the treatment, disposal or regeneration of the contaminant-loaded zeolitic forms will also definitively increase their environmental application possibilities.

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