Fresh perspective on the use of natural zeolite in the chemical industry and environment

Mansour Jahangiri* , Amir Ebrahimi, Ali Aminian
Chemical, Oil and Gas Engineering Department, Semnan University, Semnan
*Jahangri@gmail.com

Abstract

The application of natural zeolitic materials to the reduction of heavy metals and petroleum products has been studied. This contribution provides 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]. 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. 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.

2. The practical use of zeolite to the environmental restoration projects

The application of natural zeolites to the environmental remediation is mainly based on their ion-exchange properties. 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 [2]. Equilibrium data relative to exchange reactions between these zeolites and various toxic and noxious cations, namely Cd^{2+}, Pb^{2+}, Cu^{2+}, Zn^{2+}, Cs^{+}, Sr^{2+}, Ba^{2+}, Co^{2+}, NH_4 , and two representatives of alkaline and alkaline-earth cations, such as K^{+} and Ca^{2+}, are critically reviewed. Experiments 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 [3]. 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.). It is worth mentioning that the use of natural zeolite (clinoptilolite) has considerably reduced the 137Cs and 90Sr levels [4]. Clinoptilolite efficiently adsorbed Cu^{2+}, Fe^{2+}, Al^{3+}, and Zn^{2+} within 20–30 min. Stability tests were carried out for pH from 1 to 5 to determine the leaching of ions from clinoptilolite. After acid treatment at pH 2, the clinoptilolite released significant amounts of Al, Fe, Na and K cations. XRD patterns revealed that clinoptilolite treated at pH 1–5 for 144 h had similar diffraction patterns and minimal change in crystallinity. Zinc uptake by adsorption from zinc-spiked acid rock drainage (ARD) on natural clinoptilolite was investigated in a slurry bubble column. The effects of contact time, adsorbent particle size, initial aqueous zinc concentration, adsorbent dosage and initial solution pH on zinc immobilization were examined. Zinc adsorption improved as pH increased from 2 to 5, probably due to competition of H^{+} at low pH. A slurry loading of 200 g clinoptilolite per kilogram ARD and an initial aqueous pH of 4 appear to be suitable conditions for removing zinc from ARD. 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 [5]. The regeneration of the zeolites by a number of solutions was also investigated in some cases. Natural zeolite was added to artificially polluted garden soil to immobilize and limit the uptake of lead by rape through changing soil physical and chemical properties in the pot experiment under greenhouse conditions. Results indicated that the addition of natural zeolite could increase soil pH, content of soil organic matter and promote formation of soil aggregate. Data obtained suggested that the application of a dose of zeolite was adequate (≥10g kg−1) to reduce soluble lead significantly, even if lead pollution is severe in garden soil (≥1000mg kg−1. 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. 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 [6]. The purification of waters and the treatment of industrial and urban wastewaters are further fields of applications of natural zeolitic materials. Natural zeolite was used as a low-cost adsorbent to evaluate its ability to remove color from effluents. Natural zeolites were mainly investigated and applied as sorbents for ammonium from urban as well as for heavy metals and dyes from industrial wastewaters.

3. Perspective on the use of natural zeolites and 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. [7]. 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. The in situ microbial regeneration of permeable reactive of barriers was also investigated. 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 [8]. 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. 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 [9].

4. Conclusions

The sorption capacity of the raw and modified natural zeolites cannot be compared with 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. 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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