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Review

Trends and Perspectives Regarding the use of Natural and Synthetic Zeolite Systems in Environment Protection (Review)

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Abstract

The zeolite material that is available nowadays for the confection of devices and systems that are used in environment protection is represented by an ensemble of natural modified zeolites and synthetic ones that ensure the adsorption of various pollutants. Natural zeolites facilitate ion exchanges, absorption and catalysis, these proprieties securing their use as protectors and restorative for polluted water, soil and plants. The modification of zeolites is represented by a transformation of the natural zeolite into cheaper adsorbent materials that are very efficient in the purification of environments that have been polluted with heavy metals. This review summarises the application of natural and modified zeolites in the protection and decontamination of the environment.

Keywords: Decontamination, Devices, Environment, Protection, Systems, Zeolite

INTRODUCTION

Zeolites that are found in the volcanic tuffs are part of the tectosilicate class. They are hydrated aluminosilicates of calcium and sodium mainly. Natural zeolites are formed over millennia through the sedimentation of volcanic ash in salt water lakes, alkaline sediments of lakes and soils from the desert or in marine sediments and metamorphic rocks. These environments facilitate the chemical reactions of zeolite ash and alkaline water. The volcanic tuff was documented for the first time by the Swedish mineralogist, Freiherr Axel Fredrick, who also named it "zeolite" because after being heated, it produces a large quantity of steam ("zeo" comes from Ancient Greek and it means "hot stone" that eliminates water when heated. Two decades ago, Marcus and Cormier (1999) stated that there are over 40 types of natural zeolites and over 150 types of synthetic zeolites. More recently, Monte and Resende (2005) have stated that there are over 80 types of zeolites known and a few hundred synthetic zeolites. In the past, only natural zeolites were used, but nowadays synthetic zeolites are exploited as well because they are easy to obtain and use. Synthetic zeolites are widely spread around the world and China is considered to be the biggest zeolite producer and consumer. Due to their universal use in various fields and their global presence, zeolites are amongst the most appreciated natural resources (Hrenovic and Tibljas, 2002; Pogurschi et al., 2016; Vrzgula et al., 1988).

Important mineral deposits formed only a few types of natural zeolites (analcime, chabazite, clinoptilolite, natrolite, heulandite, stilbite, phillipsite) and the most widespread is clinoptilolite (USA, Russia, China, Bulgaria, Macedonia, Croatia, Bosnia and Herzegovina, Japan). Romania has important zeolite natural resources, especially clinoptilolite from Rupea, Brașov (Popa et al., 2017). There are numerous quarries in Cluj County situated in Aluniş, Apahida, Borşa, Cuzdrioara, Iclod, MăguraCaşeiu, Nima, OcnaDejului, Rupturi, Ţigla (Bedelean et al., 2006; Ulmanu et al., 2006).

Environment pollution continues to be a current and important issue that will impact the future of global civilisation. Nowadays enormous quantities of inorganic and organic pollutants accumulate and they are very harmful for the environment. This fast rate of pollution is due to the continuous growth of urban population and implicitly transportation, industrial and energy production, uncontrolled intensified and chemically oriented agriculture, the repercussions of the nuclear accident and the nuclear waste storing facilities. When the pollutants concentration exceeds some ranges, their presence jeopardises the environment and public health so correction strategies are needed. Corrective procedures are mainly based on the extraction of the pollutants from the soil and water systems or by mobilizing and in situ stabilization (Shi et al., 2009). Over time many materials and techniques were used in de-polluting the ambient. Among them, natural and synthetic zeolites are very popular materials used for decontamination. Natural and synthetic zeolites established themselves because of their advantages such as their global availability, low cost, mechanical and thermic proprieties correlated with a high absorption rate and soil and water pH regulating system. On the other hand the use of natural zeolites does not represent a supplementary pollution source for the environment. This review aims to update the applications of natural zeolites and some other modified types of zeolites regarding the potential of these compounds to bind and chemically stabilize various industrial and common pollutants (inorganic, organic and radioactive) from soils, water and other sources, in order to develop new procedures for the protection of the environment.

The use of natural zeolite based materials for environmental protection

The pollution of the environment continues to rise in alarming rates and to gain new connotations. In this regard it is important to note one of the most recent and alarming sources of pollution in Romania generated by the increase in the levels of some heavy metals (Fe, Mn, Zn, Cu, Pb, Cd, Ni) and the pH levels of the water in the Someș and Tisa drainage basins after a few mines from Maramureș were closed (Smical et al., 2015). In order to reduce the heavy metal pollution zeolites are frequently used because of their efficient absorption capacities. In this context it is appropriate to evaluate the efficiency of natural zeolites to decontaminate heavy metal polluted soils and plants because these volcanic tuffs reduce the transfer of heavy metals into the cultivated plants and spontaneous flora. Ulmanu et al. (2006) evaluated the capacity of a zeolite from Baia-Mare to retain some heavy metals (lead, copper, zinc, cadmium and manganese) from soil and a few cultivated plants (corn, mustard plants and oats). The first table shows the physical characteristics (the specific surface is measured using the BET N_2 adsorption method), mineral characteristics (determined using X-ray diffraction method) and chemical properties of this type of zeolite. After conducting this research, the authors determined that Baia-Mare zeolites had decreased the lead, copper, cadmium and manganese transfer in corn, mustard plants and oats. The study also stipulated the fact that the efficiency of the reduction of the transfer of these heavy metals from soil into plants was directly proportional to the zeolite concentration. It is also important to mention the results from commercial research and documentation that evaluate the quality of Rupea zeolites, an important natural resource of Romania. Their unique characteristics are presented in the specification sheet provided by S. C. Zeolites Group, where the physical, chemical and mineralogy characteristics are presented (Table 2).

Characteristics and action principles of zeolites used in the environmentprotection

Volcanic tuffs from Romania are rich in zeolites and usually have a vitroclastic texture. Clinoptilote is the most commonly found type of zeolite together with modernite, phillipsite, analcime and other secondary minerals (quartz, calcite, muscovite, biotite and plagioclase). Natural zeolites are used in various fields because of their structural and physicochemical characteristics such as: low density, adsorption, ability to perform ionic exchange, molecular sieve, catalysis, hyperhydration; they can easily dehydrate and consequently form voluminous holes, the stability of the crystalline network after dehydration and the ability to form molecular channels in the dehydrated crystals. All of these proprieties can be influenced by numerous factors such as: the characteristics of the mineral, pH levels, temperature, impurities, the cationic properties of heavy metals, the circumstances of application, pore clogging and the size of the particles. It is important to mention the fact that these factors can have a major impact on the sorbent capacity of zeolite materials used in systems designed for environmental decontamination. Therefore the use of natural zeolites in soil and water decontamination is completely justified. The vast majority of water decontamination technologies that use zeolites are based on their ability to facilitate cationic exchange.

The dissolved cations can be removed from the water through the exchange with other cations that are part of the zeolites (Varvara et al., 2013). It is important to mention that there were some experiments conducted regarding some devices based on bio augmented silt and natural zeolites that remove phosphorus (Montalvo et al., 2011). Regarding these devices, phosphorus absorption is due to the bioactivity of the bacteria-rich slurry: phosphate accumulating bacteria precipitate phosphate, which in turn, is absorbed by the zeolite and then suspended in the purifying solution (Montalvo et al., 2011). Similar principles lay at the basis of other experimental methods in order to remove arsenate and arsenite from drinkable water (Neamţu et al., 2016). It is important to mention the review paper by Koshy et al. (2016) regarding zeolite application in water and soil decontamination that highlights the use of permeable

Table 1. The mineral, physical and chemical characteristics of Baia-Mare zeolites (Ulmanu et al., 2006)

Parameter	Value
Main component - clinoptilolite	Up to 80%
Quartz	4 - 5%
Feldspat	3 - 4%
Mordenite	1- 2%
SiO_2/Al_2O_3 ratio	5.6
Surface (B.E.T, m^2/g)	52.0165 ± 0.2833
External surface(m^2/g)	45.7051
Micropore surface (m^2/g)	6.3115
Micropore volume (cm^3/g)	0.002466
Pore diameter (mean value), Å	101.8246
CEC (meq/g)	1.5105
SiO_2 (%)	64.58
Al_2O_3(%)	11.49
CaO (%)	1.19
MgO (%)	0.33
Na_2O (%)	2.50
K_2O (%)	2.55
Fe_2O_3 (%)	1.31
H_2O (%)	12.92
Other (%)	3.13

Table 2. Physical, chemical and mineral characteristics of Rupea zeolites (S.C. Zeolites Group)

Physical characteristics		Chemical characteristics (%)		Mineral characteristics (%)	
Softening point (°C)	1250	SiO_2	68.75 -71.3	Clinoptilolite	87-90
Melting temperature(°C)	1320	Fe_2O_3	1.90 -2.1	Plagioclase	2-5
Melting flow temperature (°C)	1400	Al_2O_3	11.35 -13.1	Anherit	2-3
Color	gray-green	MgO	1.18 -1.20	Cristobalite	4-5
Smell	odourless	CaO	2.86-5.2	Clinoptilolite	87-90
Porosity (%)	32-44	Na_2O	0.82-1.30	Plagioclase	2-5
Pore diameter (nm)	0.4-0.6	K_2O	3.17-3.40	Anherit	2-3
Durity – Mohs scale	3.5 - 4	P.C	8.75-8.86	Cristobalite	4-5
Water absorption (%)	34 - 36	SiO_2	68.75-71.3		
pH	8.75	Fe_2O_3	1.90-2.1		
Density	2.377				

reactive barriers to decontaminate wastewater. Zeolites can absorb and retain up to 60% of the weight of water and even alcohol because of its porous constitution (Burmanczuk et al., 2015; Zhang et al., 2013). Water molecules that can be found in the porous structure of zeolites can evaporate without damaging the structure of the volcanic tuff. Consequently zeolites ensure a permanent water reservoir, maintaining humidity during arid periods of time. The efficacy of the absorption process of zeolites of petroleum products in gaseous and water environments has been heavily studied and the obtained results made it possible for zeolite materials to be recommended as adsorbents for various hydrocarbons (Mishra and Jain, 2011; Micle et al., 2018; Passaglia et al., 2005). Of utmost importance are the results of different experiments that have proved the adsorbent effect of clinoptilolite for lead, aluminium, zinc, iron, caesium and especially cobalt from residual waters (Neag et al., 2020; Wen et al., 2018) The removal of nuclear waste and dangerous residues is another important priority in the use of zeolites (Cătuneanu et al., 2010; Luz, 1995; Simical et al., 2015; Vignola et al., 2011a; Vignola et al., 2011b). There is a multitude of research conducted around the use of zeolites as filters and permeable barriers for the decontamination of subterranean water and other types of residual water. Zeolites filters (with ZSM-5 and modernite) have been used for a long period of time to purify subterranean hydrocarbon and inorganic salts polluted waters (Vignola et al., 2011a).

The main applications of natural zeolites in the environment protection

Zeolites have been used in environmental activities ever

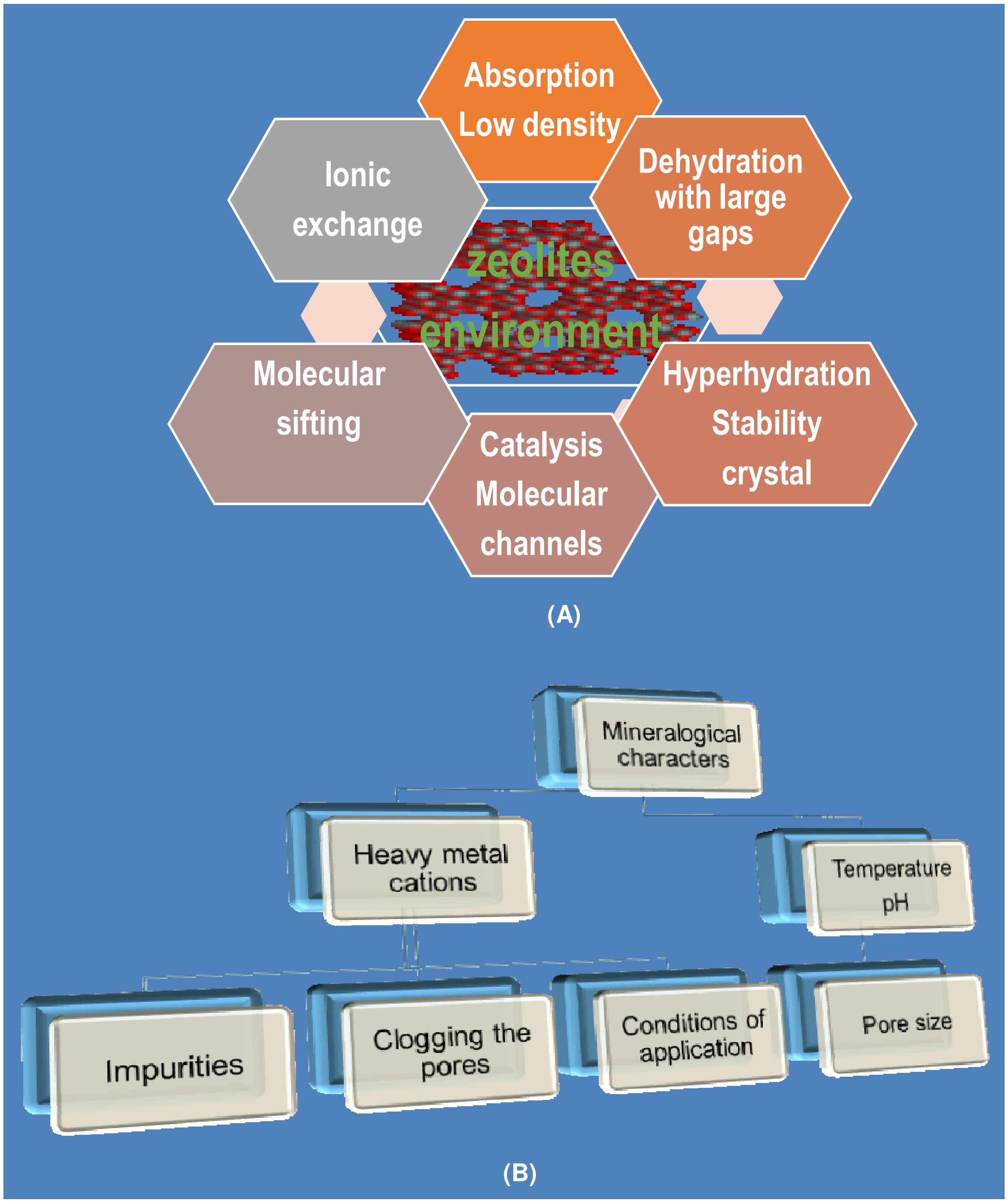

Figure 1. The main structural and physicochemical properties that stand at the basis of the use of zeolites in environmental protection (A) and factors that influence their de-polluting potential (B)

since the 1950s', the first zeolitic material used was clinoptilolite as an ammonia removal agent in order to reduce the pollution and facilitate selective ionic exchange (Ames, 1960). Over time zeolites proved to be useful in various fields of environmental protection of which of great importance are the filtration and purification of residual and radioactive water, the decontamination of soils and the removal of gas or unpleasant smells (Mumptonși Fisherman, 1977; Inglezakis and Zorpas, 2012).

Nowadays clinoptilolite is the most used natural zeolite because it has important applications in the protection of the environment due to its adsorbent, catalysis and ionic exchange properties. Figure 1

Out of the many uses of clinoptilolite it is important to mention: the decontamination of waste water, water demineralization and purification, processes that are already being used in many European cities; the reduction of petrochemical pollution through the separation and removal of the pollutants, gases and solvents (Lee and Valla, 2019); soil sanitation and disinfection (Misaelides, 2011); radioprotection and the reduction on radioactive pollution.

Regarding the radio protective action of zeolites it is

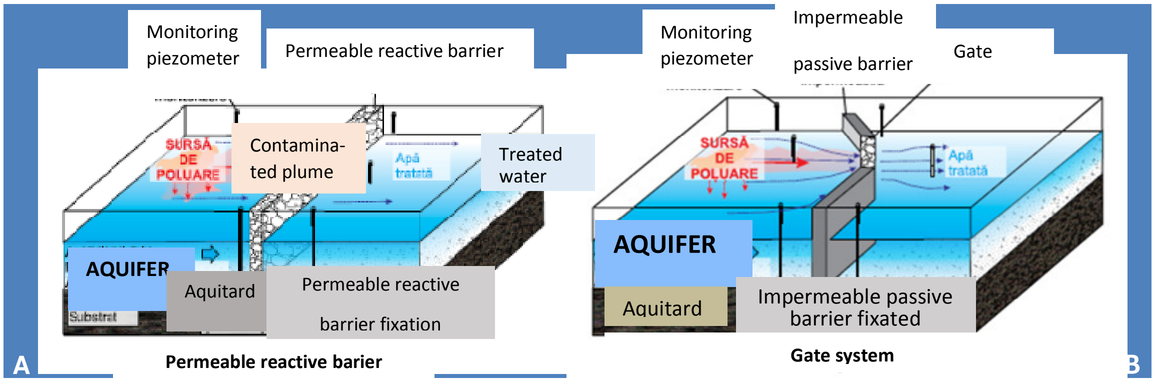

Figure 2. Graphic representation of a classic PRB system (A) and of a "door" type barrier (B) (Colombano et al, 2006).

important to mention the measures taken after the Chernobyl nuclear explosion that was based on the radio protective actions of clinoptilolite; 500.000 tons of clinoptilolite were used for radio protection, of which a big quantity was used to make a protective sarcophagus around the reactor and the other part was used to decontaminate water resulting in a significant reduce of ^{131}Cs and ^{90}Sr pollution (Mumpton, 1999).

*Permeable reactive barriers (PRB).*In order to make a PRB it is very important for it to be attached to an impermeable substrate situated in the inferior layers of the soil so that the pollutants cannot reach under the barrier (Figure 2). The vast majority of the PRB is anchored at depths situated between 10 and 20 meters, which helps maintain a correct sizing and it does not need the reactive material to be replaced during the correction process. PRB usually consist of a permeable part that contains reactive materials (reactive metals, acceptors and electron donors, adsorbents, bacterial bed) that is situated over a subterraneous source of polluted water. Therefore, as it can be seen in Figure 2, the natural flow through a purifying barrier of the water is ensured in order to provide the decomposition of pollutants into non-toxic (organic) elements or they can be adsorbed (organic pollutants, metals and metalloids) by the reactive components (Colombano et al, 2006). PRB are based on making a trench of which its dimensions should permit the interception of the whole polluted body of water. A good interception is achieved when the PRB is positioned on the direction of the natural flow. The volume of the reactive components can vary from a few meters to hundreds of cubic meters. Based on the reactive materials used we can establish tree major types of PRB:

- Sorption barriers that are based on the use of zeolites or coal as adsorbent materials that need to be changed after they are saturated. This barrier is usually used for organic compounds (Liu et al, 1996);
- Precipitation barriers that use as reactive materials lime related compounds that react with the contaminates represented mainly by inorganic compounds;
- Degradation barriers that use iron fillings as reactive materials that can decompose some organic pollutants into less toxic or non-toxic compounds.

Another important characteristic of PRB is their composition with materials made of nutrients, oxidants and reducing compounds that create the propitious hydro geochemical environment in order to decompose some organic pollutants (Rangnekar et al., 2015; Băbău et al., 2018). Vignola et al. (2011a; 2011b) periodically evaluated the performances of zeolites used for a year as adsorbent materials in PRB situated under a coastal refinery. There were conducted a series of analysis on the composition of the wastewater and on the contaminants that were located in the zeolite channels. The authors have found that the concentration of the organic contaminants in the evacuated water was within the normal range. The pumping treatment technology is another method used to decontaminate subterraneous water. It is not as efficient as PRB especially in chlorinated hydrocarbons and aromatic hydrocarbons contaminated water. As an alternative for the pumping treatment technology PRB represents an adequate solution in order to efficiently decontaminate subterraneous water (Vignola et al., 2011a; Vignola et al., 2011b).

The use of modified zeolites in the protection of the environment

Modified zeolites are a special and new category of absorbent materials used to the protection and decontamination of the environment. Of great interest are surfactant-modified zeolites. Surfactant-modified zeolites are adsorbent materials that have cationic absorbent properties; thus, they have an improved capacity to adsorb anionic substances and pathogens from the wastewater. Zeolite materials are used as decontami-nation agents for soils and water, as filling and sealing materials for waste deposits and as permeable reactive barriers for water purification (Bowman, 2003). The modifying agents are usually quaternary amines that form a structure on the surface of zeolites a stratified structure thus changing their surface electric charge (from a negative charge to a positive one).The positive electrical charge of the surface provides better adsorption for anions and at the same time the newly formed structure will absorb the organic nonpolar compounds (Misaelides, 2011). It is also important to mention the research that proved the fact that surface-active modified natural zeolites can efficiently bond to various anionic metals (chromates, iodides, nitrates and perchlorides) (Wingenfelder et al., 2006). It has been proven that surfactant enriched modified natural zeolites are efficiently used to treat wastewater that comes from oil fields and absorb volatile hydrocarbons (benzene, toluene, ethylbenzene and xylenes) (Misaelides, 2011). On the other hand, zeolites are good bacterial transporters and they considerably improve the action of the silt used in sewage plants. A major disadvantage of these applications is due to the slow forming of the bacterial layer on the surface of zeolites. This delays its efficacy by almost a week. Surfactant enriched modified natural zeolites also have the capacity to bind with pathogens such as *Escherichia coli* (Al-Nasser et al., 2011; Bowman, 2003).

Environmental remediation is another important application of natural and modified zeolites because of their ionic exchanges properties that consist of the release of cationic locus in order to facilitate anionic absorption (Misaelides, 2011). Misaelides (2011) suggested the implementation of treatments that are based on cleaning and regenerating the zeolite materials filled with contaminants, thus improving the potential and the duration of use of the materials (Trgo and Peric, 2003). It is also important to mention that there were studies that investigated the catalytic effect of some zeolite materials with medium-sized pores (H-ZSM5), large-sized pores (HY) and zinc modified zeolites (Trgo and Peric, 2003). H zeolites were prepared using calcination (at 550 ^{o}C) and ammonium nitrate methods and for the zinc modified zeolites moisture impregnation zinc (Ugal et al., 2010). It is considered that by modifying natural zeolites, superior results are obtained because their action and selectivity are improved.

CONCLUSIONS

There is no significant difference between the structure and properties of natural and modified zeolites which explains the similar adsorbent qualities of these materials. Even though natural zeolites have good adsorption properties their use is limited due to their high costs, especially when used for decontamination systems that require a large quantity of the volcanic tuff. The information provided by academic and industrial research provide new perspectives regarding the development of new technologies in the protection of the environment in order to optimise PRB and other technologies that are already being used for depollution. Local and national communities that are involved in the protection of the environment promote the use of adsorbent materials that have a good chemical and physical stability, qualities that are scientifically proven in the case of natural and modified zeolites.

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