

K. Kędziora, J. Piasek, J. Szerement, A. Ambrożewicz-Nita  
Institute of agrophysics PAS, Lublin, Poland

## USE OF MODIFIED ZEOLITE IN ENVIRONMENTAL ENGINEERING. A REVIEW

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**A review of literature concerning application of natural and modified zeolites for water and wastewater purification from inorganic (ionic) and organic pollutants is presented.**

**Key words: zeolites, purification, pollutants.**

**Подано огляд літератури з питань застосування природних і модифікованих цеолітів для очищення води і стічних вод від неорганічних (іонних) і органічних забруднювачів.**

**Ключові слова: цеоліти, очищення води, забруднювачі.**

### Introduction

The main cause of water resources degradation is industrial and municipal wastewater discharge occurring at so-called pollution points and characterized by high levels of pollutants. The highest threat to groundwater contamination comes from industrial water deposits and agricultural land, on which the fertilizers and protection products are applied. The greatest danger of water races are compounds derived from household wastes, manure and industrial waste water. Extremely dangerous chemicals are synthetic detergents, which are not biodegradable and compounds of cadmium and lead, commonly used in industry (World Health Organisation, 2006). In Poland water quality assessment based on monitoring the purity of rivers managed by the Regional Inspectorate for Environment Protection classifies over 5,5 % of water as very severely polluted (Główny Inspektorat Ochrony, 2010). To minimize the impact of pollution on surface water and land apply of wastewater treatment must be conducted. Constantly ongoing research show more and more opportunities to use natural and modified zeolites to purify wastewaters and environment protection, because of their unique molecular-sieve, sorption and ion exchange properties.

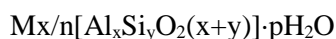
Surface deposition of sedimentary zeolites, and their relatively easy mining creates excellent conditions for their wider use (Ciciszwili et al., 1990). Their global resources have not yet been exactly estimated, but zeolite sources in areas of young volcanism (Iran, Japan, New Zealand) are well recognized (Bolewski, 1994). Zeolites are common in igneous, metamorphic and sedimentary rocks (D. Różycka, 1997). The main groups of zeolitic deposits are in alkaline lakes, salt pans and alkaline soils. Kind and content of zeolites depend on the structure and composition of the surrounding rocks, their geological age, composition and temperature of surrounding water (Bolewski, 1994).

In Europe, Hungary uses deposits of zeolites on a largest scale. Mining industry is well developed in Bulgaria, Slovakia, Yugoslavia and Ukraine (Różycka and Stehman, 1997). The most widespread and creating the greatest resources is clinoptilolite, belonging to a heulandite group (Ciciszwili et al., 1990). Its unique sorption and ion exchange properties, at a relatively low price, determine its universal use in many industries, agriculture and environmental protection. It can be successfully used to remove heavy metals, nitrates, phosphates and organic pollutants from wastewater (Piaskowski and Anielak, 2000).

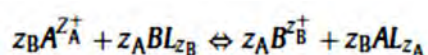
The aim of this paper was to show the use of natural and modified zeolites for purification of wastewater.

### Natural zeolites and cations adsorption

There are many natural zeolites identified in the world. Clinoptilolite, mordenite, phillipsite, chabazite, stilbite, analcime and laumontite are very common forms whereas offretite, paulingite, barrerite and mazzite, are much rarer. Among zeolites, clinoptilolite is the most abundant natural mineral. The general chemical formula of zeolites is



where M is (Na, K, Li) and/or (Ca, Mg, Ba, Sr), n is cation charge;  $y/x = 1-6$ ,  $p/x = 1-4$ . The tetrahedron is the primary building unit of zeolite framework, the centre of which is occupied by a silicon or aluminium atoms, with four oxygen atoms at the vertices. Substitution of  $Si^{4+}$  by  $Al^{3+}$  defines the negative charge of the framework, which is compensated by monovalent or divalent cations located at the surface. The aluminosilicate framework, defining the structure type, is the most stable component. Water molecules can be present in voids of large cavities, bonded between framework ions and exchangeable ions via aqueous bridges and as bridges between exchangeable cations (Sprynskyy, 2012). Zeolites are capable to exchange ions with external medium, which is the most significant characteristic of zeolite. The equilibrium ion exchange is expressed by the following equation (Pollard et al., 1992)



where  $z_A+$  and  $z_B+$  are the valences of the respective cations, and L is defined as a portion of zeolite framework holding unit negative charge. The ion-exchange behavior of natural zeolite depends on several factors, including the framework structure, ion size and shape, charge density of the mineral network, ionic charge and concentration of the external electrolyte solution (Bish and Ming, 2001). Due to the environment factors during mineral formation, natural zeolite has varying chemical composition and cation-exchange capacity (CEC). Usually high CEC values of zeolites are reported, however values between 0.6 and 2.3 meq/g were found by Shaobin Wang, 2010. Permanent negative charges on natural zeolites and cation exchange reactions enable their high ability to bind cationic pollutants but little or no affinity for bind anions (Wang and Peng, 2010).

Lethality of heavy metals for living organisms (tumors, organ harms, sensory system harms, and fatal outcomes) is commonly recognized (World Health Organisation, 2006). Removal of heavy metals from wastewaters incorporates coagulation, carbon adsorption, particle trade, precipitation, reverse osmosis, and others (Barakat, 2011). Zeolites have been used for heavy metals immobilization from natural or industrial water. The use of numerous natural and modified zeolites for the uptake of heavy metals from variety of synthetic and real wastewater was amazingly increased in the last few decades (Leyva-Ramos et al., 2008; Baskan, Pala, 2011; Wingenfelder et al., 2005; Guibal, 2004; Oliveira, Rubio, 2007; Barakat, 2011; Malekpour et al. 2011; Jiménez-Cedillo et al., 2009; Doula, 2009; Curkovic et al., 1997). It is realized that the immobilization of heavy metals from aqueous solutions by zeolites is truly a confounded process, comprising of adsorption and precipitation of metal hydroxides on dynamically changing localities of the molecule surface and depends on the kind, and grain size of zeolite used, contact time, pH, temperature and initial metal concentration.

### Modified zeolites and anions adsorption

Agricultural, municipal or industrial wastewaters are characterized by excessive nitrate concentrations, much higher than 50 mg/L (European standard of drinkability), which leads to several defects towards the human health and the ecosystem, with the anarchic growth of aquatic plants and algae (eutrophication) (Levine and Schindler, 1989). Various methods have been reported for the removal of nitrate from water and wastewater, including biological denitrification (Park et al., 2009), chemical reduction (Li et al. 2010), reverse osmosis (Schoeman and Steyn, 2003), electro dialysis (Menkouchi Sahli et al., 2008) and/or adsorption (Karimi et al., 2010). Among these methods, adsorption is generally considered to be the simplest and enough efficient method.

An interesting materials, extending the area of application in wastewater treatment to anions sorption are surface-modified zeolites among which surfactant-modified zeolites (SMZ), polymer-modified zeolites (e.g. by polyhexamethyleneguanidine) (Shoumkova, 2011) metal cation-modified zeolites and oxides modified zeolites can be distinguished (Świdarska-Dąbrowska, 2011; Anielak, 2011). Such materials combine the cation sorption properties typical for zeolites, with the ability to absorb anionic species (e.g. nitrates, phosphates, arsenates, chromates, iodides, perchlorates, antimonates) and non-polar organics (e.g. benzene, toluene, ethylbenzene, and xylenes (BTEX), phenoles, pesticides, herbicides, dyes, etc.). The most frequently used surface-charge modifying agents are quaternary amines (e.g.

hexadecyltrimethylammonium (HDTMA), cetyltrimethylammonium bromide (CTMA), octadecyldimethylbenzyl ammonium (ODMBA), N-cetylpyridinium (CPD), benzyltetradecyl ammonium (BDTDA), stearyldimethylbenzylammoniumchloride (SDBAC), all forming bilayer structures on the zeolite surface (Shoumkova, 2011). The positive charge of these species adsorbed on zeolite surface provides surface sites for sorption of anions, and the organic surface layer provides a partitioning medium for sorption of non-polar organic compounds (Shoumkova, 2011). Modified zeolites besides anion exchange properties, keep the ability to adsorb inorganic cations as well, because the modifiers are relatively large molecules and remain on the external surface of the zeolite crystals and do not enter zeolite channels (Northcott et al., 2010). The SMZ are stable in water and aggressive chemical solutions (Basaldella et al., 2006). Cationic surfactants molecule is composed of a hydrophilic and positively charged head group and a hydrophobic tail (Wang and Peng, 2010). Sorption of cationic surfactant can be described by general model: external surface of zeolite is covered by a surfactant monolayer ("hemimicelle") via strong Coulombic interactions at surfactant concentrations lower than the critical micelle concentration (CMC) and then at surfactant concentration equal to or above CMC, a next layer of surfactant molecules (admicelle) is attached to the previous layer via hydrophobic interactions. This second layer formation results in a charge reversal of the external zeolite surface, providing sites where anions may be retained (Leyva-Ramos et al., 2008).

The most popular oxide-modification of zeolites is iron (hydr)oxides treatment which simple, effective and relatively inexpensive, however it needs calcination at rather high temperatures. Świdarska-Dąbrowska (2011) obtained the best Fe-modifications results at 450 degrees, (point of zero charge at pH 7 and high values of the zeta potential over a wide pH range) whereas 350°C calcination resulted in lowest values of zeta potential of the activated zeolite.

Chitosan is also a promising material for nitrate sorption (Chatterjee et al., 2009). It is easily obtained by the alkaline hydrolysis of the amino groups of chitin in a strong base (Guibal, 2004). To increase low mechanical resistance of chitosan based materials, they deposition on natural zeolites was proposed (Arora et al., 2010).

Phosphates, along with nitrates, are nutrients responsible for the eutrophication of aqueous systems, which leads to short and long term environmental problems. The two most common methods for phosphate removal from wastewater are: chemical precipitation and biological treatment, however complete removal of phosphates is still unattainable by these methods, due to thermodynamic and kinetic limitation (Ning, 2008). Phosphate removal by zeolites have been obtained with a good result by using sulfate-coated zeolites. Improvement of the adsorption capacity for phosphate by coating was accomplished through ion exchange between phosphate and sulfate on the surface of the adsorbents (Choi et al., 2012).

#### **Use of zeolites for removal of azo dyes from water**

Dyes in wastewater comes primarily from textile, printing, food and leather processing. In water environments dyes decrease daylight infiltration and thus influence photosynthesis. Some dyes are dangerous or cancerogenic (Wang et al., 2005). The adsorption of dyes by natural and modified clinoptilolites was recently inspected in (Armag et al., 2003), showing that natural zeolite is not a suitable adsorbent for azo dyes due to the exclusion of the dye anions from the adsorbent pores. Zeolite modified with a typical quaternary amine surfactant (HTAB) adsorbes anionic dyes. The modified zeolite exhibits cationic charges that can react with the anionic dye sulfonate groups. The adsorption isotherms with modified adsorbents showed three regions of interest, each corresponding to a different adsorption mechanism. The adsorption in Region I is controlled by electrostatic attraction of the dye anionic groups onto adsorbed cationic head groups of the HTAB molecules. The positive zeta potential supports this mechanism. Regions II and III are attributed to the precipitation of an anionic dye-cationic HTAB complex, and the formation of solid phase of the dye, respectively (Armag et al., 2003).

#### **Use of zeolites for removal of BTEX**

BTEX are cancerogenic and have severe impact on the central nervous system. Entering of BTEX to groundwater and soil commonly happens close to petroleum and gas factories, and fuel stations and tanks. Ranck (2005) used HDTMA-modified zeolite for long-term BTEX removal showing that SMZ totally

removes BTEX from wastewater up to a compound-specific capacity, and that SMZ might be recovered by air sparkling without decrease of sorption limit. Benzene, the most soluble compound, began to elute first - at 8 pore volumes (PV), while the least soluble compounds, ethylbenzene and xylenes, began to elute at 50 PV, which was in agreement with the BTEX behavior formerly reported by Basaldella (2006). Russo (2014) found that iron oxide modified zeolite removed near 80% benzene in the relatively short time of 40 min and the process showed good stability for 250ml of processed sample. It is a very promising result for a continuous Benzene removal process. Neither Fe(II) nor Fe(III) was detected in the eluted solution.

#### **Use of zeolites for removal of phenols**

Phenols are lethal compounds originating from a variety of industrial sources, for example, pesticides, dyes, paper, coke and gum production as well as material, plastic, rubber, pharmaceuticals, and petroleum processing. Dong (2010) investigated adsorption of bisphenol A by zeolite modified with HDTMA demonstrating significantly improved adsorption capacity in respect to no modified mineral. The SMZ (modified with HDTMA) having higher BET surface area and higher amount of HDTMA exhibited greater retention of bisphenol A due to electrostatic interaction of positively charged heads of HDTMA with dissociated hydroxyls of bisphenol A, coordination of the oxygen atoms of bisphenol A by HDTMA positive charges, and the adsorption of uncharged bisphenol A via hydrophobic partitioning into HDTMA layers.

#### **Use of zeolites for removal of humic acids from tapwater**

Humic acid, fulvic acid, and humines (humic substances) are common compounds in practically all soils (Wang and Peng, 2010). Their entrance from surface and ground waters to drinking water may result in its coloring, odor and/or presence of dangerous chemicals (including adsorbed toxic elements) and thus should be reduced. Some important studies on humic substances adsorption by natural zeolites were summarized by Wang (2010). and by modified zeolite by Chunjie (2011). The latter studies showed that the adsorption of humic acid by surfactant modified zeolite (SMZFA) was very high and the maximum adsorption capacity estimated from the Langmuir model was comparable or higher than for activated carbons and clays. Adsorption of humic acid by SMZFA was enhanced at acidic pH's and in the presence of inorganic electrolyte. Since inner pores in zeolite fraction and oxides in non-zeolite part may in any case hold inorganic cations and oxyanions (e.g. phosphate), SMZFA is a potential wide-range adsorbent for water treatment to remove various contaminants with fundamentally diverse chemical properties.

#### **Summary**

The presented review shows that, due to their unique properties, zeolites have a great potential as effective sorbents for a large number of water treatment applications, such as ammonia, heavy metals phosphates, dyes and humic and/or other dissolved organic compounds from industrial wastewater, natural waters and mine drainage waters. Zeolite modification extends markedly the zeolites application. Number of different methods can be used for zeolites modification. The most common method for modification is to use organic surfactants. Low price and wide range of use in (waste)water treatment increases popularity of oxide modification. Growing interest in zeolite application in water purification is observed worldwide.

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