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APPLICATION OF NATURAL ZEOLITES AS SORBENTS IN THE CLEAN-UP OF AQUEOUS STREAMS

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Abstract

Natural zeolites can be found in volcanogenic sediments as large, widespread, mineable, near-monomineralic deposits in tuffaceous rocks. Apart of their applications as building stone, as lightweight aggregate and pozzolans in cements and concretes, as filler in paper etc., their properties as low-cost natural materials mimicking those of many synthetic counterparts are exploited in environmental protection and cleanup.

Natural zeolites found important uses in pollution control, the handling and storage of nuclear wastes, agriculture, and biotechnology. Considerable effort has made to find the most efficient ways to apply natural zeolites as an active counterpart in sorption, cation-exchange, dehydration-rehydration, and catalytic processes.

The present paper analyses some aspects of the present status of research on application of natural zeolites in environmental protection. The overview provides a short appraisal of the recent discovery concerning the natural zeolites and their modified forms in the separation, binding and chemical stabilization of some inorganic and organic in aqueous systems.

Key words: adsorption, clinoptilolite, equilibrium, ion exchange, kinetics,

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1. Introduction

The liquid streams resulted from different human activities contain various amounts of contaminants such as: suspended solids, biodegradable compounds, nutrients, pathogens, less biodegradable or persistent organic and inorganic substances such as additives, detergents, surfactants, dyes, heavy metals etc. They can show fluctuating pH, high temperature, BOD and COD concentrations in quite large limits: as a result, these effluents can pose aesthetic, environmental and health problems (Caliman and Gavrilescu, 2009; Gavrilescu and Macoveanu, 1999; Muga and Mihelcic, 2008; Tchobanoglous et al., 2004; von Sperling 2007).

During last decades, considerable advancements have occurred in treating these polluted liquid fluxes and these are reflected in major decrease in the potentially toxicity of sewage sludge

and surface waters reported, in particular in the majority of the European countries (EC, 2001; Gavrilescu et al., 2008; Krasner et al., 2009)

Several traditional processes are applied for pollutants removal from wastewater depending on their characteristics and concentrations, which can be grouped in mechanical, physico-chemical, and biological treatments (Gavrilescu, 2004; Gavrilescu, 2005; Gavrilescu and Macoveanu, 2000; Gupta et al., 2009; Kulkarni et al., 2000; Ramalho 1977; Rozendal et al., 2008; Tchobanoglous et al., 2004;

Application of most techniques, in particular biological treatment is sometimes restricted due to the essentially non-biodegradable nature of some contaminants, which should be treated by applying advanced treatment techniques: oxidation, adsorption, membrane separation, ion exchange etc. (Apostol and Gavrilescu, 2009; Betianu et al., 2008; Brinza et al., 2007; Brinza et al., 2009; Caliman and

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Gavrilescu, 2008; Caliman et al., 2008; Gupta et al., 2009; Hartmann et al., 2010; Jud and Jud, 2011; Lee and von Gunten, 2010; Lim et al., 2012; Rizo et al., 2009; Rozendal et al., 2008).

The goal of this paper is to make a short survey on the performance and application of natural zeolites as sorbents and/or ion exchangers for removal of heavy metals from contaminated aqueous streams, so as to generate the basis for experimental matter.

2. Natural zeolites as sorbents

In recent times, adsorption has gained importance as one of the most effective and comparatively low-cost methods for a wide variety of applications, especially for removal of non-biodegradable pollutants from wastewater (Crini, 2006; Han et al., 2009; Hlihor and Gavrilescu, 2009; Jovic-Jovicic et al., 2008; Otero et al., 2009). Also, adsorption processes became commercially important in the mid-1960s and the 1970s for H₂ purification, O₂ production, air purification and drying of various process streams (Ackley et al., 2003; Wang and Zhu, 2006).

At present, activated carbon is assumed to be the most effective adsorbent. However, high cost in production and regeneration make it too expensive (Abuzaid and Nakhla, 1996; Henschel, 1998; Robinson et al., 2001; Shepherd, 2001; Wang and Zhu, 2006). Natural sorbents gained the interest of scientists in a large range of applications, as low-cost sorbents. The natural microporous materials are applied as solutions of problems related to the toxic and nuclear waste management, water pollution control and decontamination, environmental catalysis, for new materials for energy storage and agricultural management (Misaelides et al., 1999; Misaelides, 2011; Wang and Zhu, 2006).

Zeolites are a large group of natural and synthetic hydrated aluminum silicates. They are natural, which offer only a limited range of atomic structures and properties, and synthetic, with a wider range of properties and larger cavities than their natural counterparts (Barrer, 1978; Pansini, 1996).

For nearly 200 years since their discovery in 1756, geologists considered the zeolite minerals to occur in nature as a result of the chemical reaction between volcanic glass and saline water, when temperatures favoring the natural reaction range from 27°C to 55°C, and the pH 9-10 (Mumpton, 1999). A zeolite is known as a crystalline aluminosilicate with a cage structure, whose framework encloses cavities (or pores) occupied by cations and water molecules with considerable freedom of movement, allowing ion exchange and reversible dehydration. The zeolite structure consists of an assembly of [SiO₄]⁴⁻ and [AlO₄]⁵⁻ tetrahedral (Fig. 1) coupled together in a variety of regular arrangements by joint oxygen atoms, to form an open crystal network containing pores of molecular dimensions into which guest molecules can enter (Mortier et al., 1982; Motti,

2010). They are considered in the class of materials known as *molecular sieves* (<http://cool.conservation-us.org/byorg/abbey/an/an20/an20-7/an20-702.html>). Zeolites occur as hydrates, and all members of the family contain at least one silicon atom per aluminum atom (Na-A Na₂O · Al₂O₃ · 2SiO₂ · 4.5 H₂O). They can accommodate sodium, calcium, or other cations (positively charged atoms or atomic clusters), water molecules, and even small organic molecules, which can be removed or exchanged without destroying the aluminosilicate framework (Trgo, 2009; Tschernich, 1992). The internal surface area accessible for adsorption ranges up to several hundred square meters per gram, and some zeolites are capable of adsorbing up to about 30 weight percent of a gas, based on the dry weight of the zeolite (Mumpton, 1983).

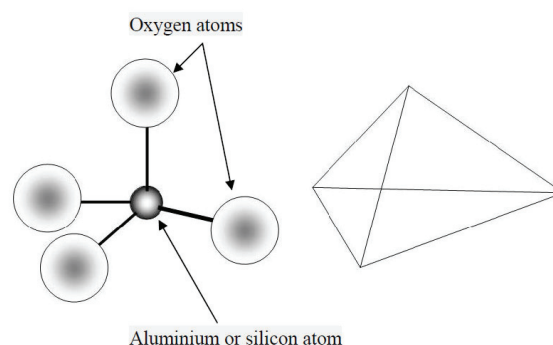
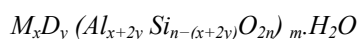


Fig. 1. The structure of zeolites unit

The general chemical formula of zeolites can be written as follows (Mumpton, 1983; Ozaydin et al., 2007):



M = K, Ca, Na, or other monovalent cations; and
 D = Mg, Ca, Sr, Ba, and other divalent cations.

Zeolites have been extensively used in various industrial applications based on their properties to act as catalysts, ion exchangers, adsorbents, detergent builders etc.) (Table 1). They can be exploited as mineral fertilizer additives, soil amendments for agricultural purposes, construction and building materials, cement additives, sorbents for oil spills, desiccant materials, water filtration adjuvants, domestic uses, carrier for pesticides, herbicides, animal feed additives, toxin binders, animal waste management, odor control, chemical spills, clean up of hazardous waste, sewage treatment, natural filtering materials for drinking and waste water treatment, nuclear remediation, a carrier for enzymes, antibiotics, glucose, sugar, and various food supplements (Muga and Mihelcic, 2008; Mumpton, 1983; Ozaydin et al., 2006).

For their chemical, physical and structural individuality, zeolites are appropriate for various applications in different areas, like adsorption of

cations, separation, ion exchange catalysis, due to their high sorption capacity and selectivity resulting from high porosity and sieving properties (Colella, 1999; Castaldi et al., 2008; Dwyer and Parish, 1983; Flanigen, 1980; Kocaoba et al., 2007; Mulligan et al., 2001). Table x describes the main properties of natural zeolites, which determine their applications. They have long been considered as outstanding candidate materials for separation and purification of gases because of their inherent ability to adsorb polar compounds (Ackley et al., 2003; Barrer, 1978). It is also known that silicates and aluminosilicates possess biological activity, either positive or negative (Bedioui, 1985; Pavelic et al., 2001). Their occurrence in Europe is illustrated in Table y (Mupton, 1983). The use of natural zeolites for environmental applications is of high interest mostly

due to their properties and significant worldwide occurrence.

There were identified about fifty different species of natural zeolites, from which only eight represent the major part of volcano-sedimentary deposits, namely: *analcime*, *chabazite*, *clinoptilolite*, *heulandite*, *erionite*, *ferrierite*, *laumontite*, *mordenite* and *phillipsite* (Ackley et al., 2003; Caputo and Pepe, 2007; Flanigen, 1980). However, only several categories of the existing natural zeolites are in sufficient quantity and purity as necessary for industrial applications.

Inside this group, *silica-rich heulandite* (*clinoptilolite*) and *mordenite* are the most relevant and play a major industrial role (Englert and Rubio, 2005; Misaelides et al., 1999; Mondale et al., 1995; Tschernich, 1992).

Table x. Properties of zeolites (Barrer, 1978; Mupton, 1983; Pansini, 1996; Trgo, 2009)

<i>Property</i>	<i>Short description</i>
Adsorption	<ul style="list-style-type: none"> - large cavities and entry channels of zeolites are filled with water molecules, under normal conditions, forming hydration spheres around the exchangeable cations; - molecules with small diameters could entry vacant channels of empty central cavities (if water is removed, usually by heating) and are readily adsorbed on the inner surfaces; - molecules too large to pass through the entry channels are excluded, generating the “molecular sieving” property of most crystalline zeolites; - the adsorption on molecular sieves is dependent on the size and shape of molecules or ions; - molecules with large polarity or polarisability can be adsorbed preferentially under identical conditions; - the adsorption process is fully reversible and of purely physical nature; - the structure of the zeolite is unchanged during the adsorption process and its later regeneration; - modifying the surface of clinoptilolite with long-chain quaternary amines allowed it to adsorb benzene, toluene, and xylene in the presence of water; - surface modified natural zeolites remove toxic compounds from animal food; - natural zeolite can be treated with amine to produce anion exchangers able of retain chromate, arsenate, selenate, and other metal oxyanions from aqueous solutions.
Dehydration-rehydration	<ul style="list-style-type: none"> - crystalline zeolites enclose reasonably narrow pore-size distributions and a uniform nature of the pores of structural cages; - natural zeolites may retain water up to 60% of their weight due to a high porosity of the crystalline structure; - water molecules in the pores could be without problems evaporated or reabsorbed without breaking the structures; - the percent of adsorption capacity is plotted against partial pressure of the adsorbate gas, according to Langmuir isotherm model
Ion-exchange	<ul style="list-style-type: none"> - the exchangeable cations of zeolites are slackly bonded to the tetrahedral framework and can be removed or exchanged; - cation-exchange capacity is a function of the degree of substitution of aluminum for silicon in the zeolite framework: the greater the substitution, the greater the charge deficiency of the structure, and the greater the number of alkali or alkaline earth atoms required for electrical neutrality, but conditioned on a number of other factors; - have a high selectivity for ammonium cations, lowering the level of ammonium in wastewaters and sewages - the zeolite beds can be regenerated and recycled indefinitely.
Biological activity	<ul style="list-style-type: none"> - natural zeolites can exhibit various biological activities being used successfully in medical therapy; - support better plant growth by improving the value of fertilizers; - improve feed conversion, reduce airborne ammonia up to 80%, act as a mycotoxin binder, improve bone density, when are used as additive in concentrated animal growing facilities
Catalytic activity	<ul style="list-style-type: none"> - zeolite catalysts have been the primary catalyst type used in refining in the last two decades; - zeolite catalysts can operate in the presence of substantial concentration of ammonia in marked contrast to other silica-alumina catalysts.

Clinoptinolite, a natural zeolite, is considered to be one of the most viable options to reduce the hazards associated with aqueous wastes (Dyer and others 1991; Kayabali and Kezer, 1998). It is the most researched of all zeolites and is widely regarded as the most useful (Ozaydin et al., 2006; Anon., 2004a).

Activated and functionalized zeolites, as powdered or flocculated forms, can be successful options in the adsorption area and the exhausted zeolites can be recycled (da Rosa Oliveira and Rubio, 2007). Activate-modify possibilities of zeolites allow various exploitation areas, such as antibacterial, antimicrobial, etc. retentions (Ozaydin et al., 2006).

3. Application of natural zeolites for the removal of heavy metals from the environment

Natural zeolites have been used in a large diversity of applications. Today, many toxic heavy metals are discharged into the environment (as industrial waste, contaminated aqueous effluents, aerosols) causing serious damages to soil, water and atmosphere (Erdem et al., 2004; Gavrilesu, 2004; Hlihor and Gavrilesu, 2009; Zospas, 2000). Heavy metals are not biodegradable and tend to accumulate in living organisms causing various diseases and disorders (Caliman et al., 2011; Hlihor et al., 2009; Kocaoba et al., 2007; Robu et al., 2007).

The two important aspects or parameter evaluation of the adsorption study are the kinetic and the equilibria of adsorption (Apostol et al., 2012; Hlihor and Gavrilesu, 2009; Kocaoba et al., 2007; Smaranda et al., 2011).

3.1. Factors affecting the retention of heavy metals on natural zeolites

The retention of heavy metals into natural zeolite was studied in order to determine their ability to uptake the metal ions from solutions with various concentrations, getting indications on the favorable sites from energetic point of view. The ions uptake (q), expressed as ions removal per unit mass of adsorbent material (mg.g^{-1}), is usually calculated from the experimental data (C_o , V , W and C_f) in each sample according to Eq. (1):

$$q = \frac{V(C_o - C_f)}{m} \quad (1)$$

where, V is the volume of the solute aqueous solution, C_o corresponds to the initial solute concentration, C_f , the final solute concentration and m is the mass of adsorbent material (Caliman and Gavrilesu, 2008; Cooney, 1999; da Rosa Oliveira and Rubio, 2007; Hlihor and Gavrilesu, 2009).

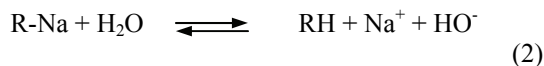
Table 1. Application of natural zeolites as sorbents for cleaning up aqueous contaminated streams

<i>Process</i>	<i>Operation</i>	<i>References</i>
Water treatment	Water filtration Heavy metal removal Swimming pools	Ozaydin et al., 2006;
Wastewater treatment	Organic compounds removal Septic leach fields Heavy metal removal Radioactive elements removal Ammonia removal from municipal sludge	Abusafa and Yucel, 2002; Bosso and Enzweiler, 2002; Cincotti et al., 2001; Englert and Rubio, 2005; Inglezakis et al., 2001; Jorgensen and Weatherley, 2003; Li et al., 2000; Rozic et al., 2000.
Agriculture	Odour control Confined animal environmental control Livestock feed additives	Filippidis, 2010; Ozaydin et al., 2006
Horticulture	Nurseries, Greenhouses Floriculture Vegetables/herbs Foliage Tree and shrub transplanting Turf grass soil amendment Reclamation, revegetation, landscaping Silviculture (forestry, tree plantations) Medium for hydroponic growing	
Household Products	Household odour control Pet odour control	Ozaydin et al., 2006
Industrial Products	Absorbents for oil and spills Gas separations	Ozaydin et al., 2006
Radioactive Waste	Site remediation/decontamination	
Aquaculture	Ammonia filtration in fish hatcheries Bio filter media	Mumpton, 1983

The heavy metal uptake is attributed to different mechanisms which include preponderantly adsorption and ion-exchange processes (Erdem et al., 2004). This is the result of the fact that each aluminum (Al^{3+}) atom substitution for silicon (Si^{4+}) in the zeolite framework generates one negative charge on the framework, so that the greater the aluminum atom substitutions, the higher the negative charges of zeolite (Nguyen and Tanner, 1998; Widiastuti et al., 2008). It was shown that metal cation sorption can occur by a combination of ion exchange, molecular sieve processes and precipitation reactions (Woinarski et al., 2006). In particular, some scientist found that clinoptilolite has a very good selectivity towards a group of heavy metals which includes: Ba^{2+} , Ca^{2+} , Cd^{2+} , Fe^{3+} , Ni^{2+} , Pb^{2+} , Zn^{2+} (Curkovic et al., 1997; Doula et al., 2002; Panayotova, 2001; Woinarski et al., 2006).

Working conditions such as the temperature, the pH of aqueous solution, the external surface activity, the presence of hydrated dissolved species and their dimensions, the presence of competing cations and other agents (complexing compounds) (Misaelides, 2011; Colella, 1999; Mondale et al., 1995) affect the sorption efficiency. The effect of temperature on the metal ions uptake is favorable, in the sense that the retention efficiency increased with increasing temperature. Curkovic et al. (1997) studied the ion exchange of some heavy metals ions by natural and modified zeolites. Their results showed that the tested zeolites included exchangeable Na, K and Ca ions, which participated in the exchange process. Also, the removal efficiency and exchange capacity is enhanced by zeolite treatment. The studies of Kragovic et al. (2012) carried out using bath natural zeolite-rich rock and Fe(III) – modified form showed that significantly higher sorption of lead resulted with the modified form. Maximum sorbed amount of lead was two times higher for Fe(III)-modified zeolite.

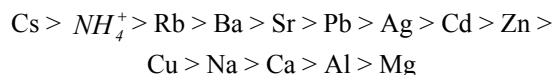
Zeolites are of weakly acidic nature and sodium-form exchangers are selective for hydrogen, depending on pH value according to the reaction (2):



When the exchanger is equilibrated with relatively dilute electrolyte solutions, this reaction can lead to high pH values (Erdem et al., 2004; Leinonen and Lehto, 2001). For example Wang and Ariyanto (2007) found that the adsorption of malachite green and Pb ions in a binary system exhibits a competitive situation during the sorption on a natural zeolite having clinoptilolite as main phase. The adsorption efficiency is reduced to 80-90%, but the total sorption is higher, and follows the first-order kinetics.

In general, the exchange potential is dependent on the electrical charge of the metallic ions and atomic weight. A possible ranking of

selectivity is illustrated below (Cabreva et al., 2005; Erdem et al., 2004):



An increase in the adsorption efficiency can occur with any increasing in pH value. However, the pH value should be maintained below that of metal precipitation (Cabreva et al., 2005).

Some researchers found that pH – adsorption edges are dependent on the metal species and zeolite concentration, and they can shift to more acidic regions if the sorbent concentration is increasing (Cabreva et al., 2005; Castaldi et al., 2008; Erdem et al., 2004).

3.2. Sorption equilibrium of heavy metals on natural zeolites

The adsorption equilibrium gives information on the amount of species adsorbed under a given set of conditions (concentration and temperature), or on the selective adsorption, which can take place when two or more adsorbable components co-exist.

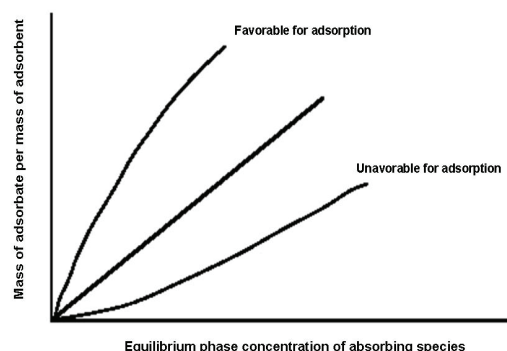


Fig. 2. Profile of sorption isotherms

Sorption data of various heavy metals have been correlated with different sorption isotherms (Table 2). The majority of studies on the rate of heavy metals ions uptake by various categories of zeolites indicated that the sorption process is generally rapid and the maximum adsorption can be found in the first hours of contact. In their study, Kocaoba et al. (2007) found that two factors could be considered as responsible for the heavy metals retention, namely: the H^+ exchange capacity of zeolites and the strength of the hydration shells of cations. From their study it was obvious that clinoptilolite is an effective and inexpensive adsorbent for Cd (II), Cu (II) and Ni (II) removal from aqueous solutions (Kocaoba et al., 2007).

The equilibrium studies of Erdem et al. (2004) carried out using a natural zeolite taken from the Enli Mining Company open pit mine in Manisa-Gördes in Western Anatolia showed that the

maximum sorption capacity of heavy metals as Cu^{2+} , Co^{2+} , Zn^{2+} , and Mn^{2+} is attained due to monolayer coverage of sorbent with sorbate.

Sorption efficiency decreases with increasing metal concentration in aqueous solutions, which indicates that energetically less favorable sites become involved with increasing metal concentrations in the solution (Erdem et al., 2004). A comparison of heavy metal adsorption capacity for some tested zeolites is presents in Table 3.

3.3. Kinetics

During the retention and exchange of ionic species on natural zeolites, a number of possible rate controlling steps can determine the process efficiency (Barrer, 1978; Inglezakis et al., 2001; Richardson and Harker, 2002):

- diffusion of counter-ions in the external solution phase surrounding the particle (film diffusion control),

Table 2. Isotherm models applied to describe equilibrium sorption processes

<i>Isotherm</i>	<i>Mathematical model</i>	<i>Linearized form</i>
Langmuir	$q_e = \frac{Q_m b C_e}{1 + b C_e}$	$\frac{C_e}{q_e} = \frac{1}{Q_m K_L} + \frac{C_e}{Q_m}$
Freundlich	$q_e = K_F C_e^{1/n}$	$\log q_e = \log K_F + \frac{1}{n} \log C_e$
Dubinin-Radushkevich	$q_e = q_D \exp(-B_D \varepsilon^2)$	$\ln q_e = \ln q_D - B_D \varepsilon^2$
Temkin	$q_e = \frac{RT}{b_T} \ln(K_T C_e)$	$q_e = B \cdot \ln K_T + B \cdot \ln C_e$
Flory-Huggins	$\frac{\theta}{C_o} = K_{FH} (1 - \theta)^{n_{FH}}$	$\log\left(\frac{\theta}{C_o}\right) = \log K_{FH} + n_{FH} \log(1 - \theta)$
Reddlich-Peterson	$q_e = \frac{K_R C_e}{1 + a_R C_e^\beta}$	$\ln\left(K_R \frac{C_e}{q_e} - 1\right) = g \ln C_e + \ln a_R$
Koble – Corrigan	$q_e = \frac{A C_e^n}{1 + B C_e^n}$	$\frac{1}{q_e} = \frac{1}{A C_e^n} + \frac{B}{A}$
Radke – Prausnitz	$\frac{1}{q} = \frac{1}{a C_e} + \frac{1}{b C_e \beta}$	-
Brunauer, Emmett, Teller (BET)	$q_e = \frac{q B C_e}{(C_s - C_e)[1 + (B - 1)C_e/C_s]}$	$\frac{C_e}{q_e(C_s - C_e)} = \frac{1}{qB} + \frac{(B - 1) C_e}{qB C_s}$
Harkins – Jura	$\frac{1}{q_e^2} = \left(\frac{B}{A}\right) - \left(\frac{1}{A}\right) \log C_e$	$\frac{1}{q_e^2} = \left(\frac{B}{A}\right) - \left(\frac{1}{A}\right) \log C_e$
Henderson	$1 - a_w = \exp(-A V^B)$	$\ln V = \{\ln[-\ln(1 - a_w)] - \ln A\} / B$

Table 3. Comparison of heavy metal adsorption capacities for the tested zeolite with other materials (upon Erdem et al., 2004; Kocaoba et al., 2007)

<i>Sorbent</i>	<i>Experimental conditions (mgL⁻¹)</i>	<i>Cu²⁺</i>	<i>Cd²⁺</i>	<i>Ni²⁺</i>	<i>q_e (mg g⁻¹), in Kocaoba et al.(2007)</i>
Clinoptilolite	Ce: 1x10 ⁻³	1.8x10 ⁻⁵			2.5x10 ⁻⁵
Philipsite		1.9x10 ⁻³			(pH 5-6)
Charbazite		4.0x10 ⁻⁵			
Analcime		9.5x10 ⁻⁵			
Scolecite	Co: 4.7x10 ⁻⁴	6.7x10 ⁻⁵			2.5x10 ⁻⁵
	Co: 2.3x10 ⁻⁴	3.2x10 ⁻⁵			9.0x10 ⁻⁶
	Co: 5.1x10 ⁻⁴	1.5x10 ⁻⁵			1.1x10 ⁻⁵
	pH: 6				
Bentonite	Ce: 1x10 ⁻³	3.0x10 ⁻⁵			2.5x10 ⁻⁵
					pH 5-6
GAC Darco	Ce: 2.5x10 ⁻⁴	8.0x10 ⁻⁵			2.5x10 ⁻⁵
	pH>6				
GAC Sharlau	Ce: 2.5x10 ⁻⁴	2.6x10 ⁻⁵			2.0x10 ⁻⁵
	pH>7				

- inter-diffusion of counter-ions within the exchanger itself (particle diffusion control),
- chemical reaction at the sites of the functional group within the exchanger (chemical reaction kinetic control).

In order to examine the controlling mechanism of sorption processes several models have been proposed: the pseudo-first-order kinetic model suggested by Lagergren for the sorption in solid/liquid systems, pseudo second-order kinetics, intraparticle diffusion kinetics (Caliman and Gavrilescu, 2009; Ho and McKay, 1998; Smaranda et al., 2011). A general solution for adsorption kinetics which includes mass transfer effects, interference effects and non-linear complex isotherms is still not available (Do, 1998; Markovska et al., 2006).

Some results of the kinetic studies proved that the adsorption reaction is of first order with respect to the metal ion concentration in solution (Eligwe et al., 1999). The rate data on the uptake kinetics of cobalt and selenite studied by Papelis et al. (2004) were analyzed based on the diffusion model, and a linear isotherm was employed for the local equilibrium correlation. The shapes of the kinetic curves for the systems Zn(II) – granular activated carbon and Zn(II)–natural zeolite with varying initial Zn(II) concentration in the range 50–250 mg dm⁻³ reported by Markovska et al., (2006) show that the sorption occurs in a two-step mechanism, but the adsorption of Zn(II) onto the natural zeolite seems to occur mainly by an ion-exchange mechanism.

4. Some applications of zeolites for heavy metals removal

Some of studies have been carried out using zeolites for the removal of heavy metals from lakes, streams, and dams (Diale et al., 2011; Hendricks, 2005; Motsi, 2010; Vaca Mier et al., 2001).

The removal of heavy metals, such as Fe, Pb, Cd, Zn from acid mine drainage is an important field for applications of natural zeolitic materials in the view of their removal from aqueous streams (Misaelides, 2011; Motsi, 2010). The application of natural zeolitic materials to the reduction of heavy metals and petroleum products in motorway stormwaters was also considered by Pitcher et al., (2004). The ion-exchange equilibrium of Pb(II) and Cd(II) on clinoptilolite from different deposits was studied by Berber-Mendoza et al. (2006).

The excellent sorption capacity, smoothness, thermal conductivity, chemical stability, mechanical strength, determine the suitability of the natural and modified zeolitic materials, along with the clays, for utilization as liners barring the dispersion of the contaminants in permeable reactive barriers (Jovic-Jovicic et al., 2008; Lai et al., 2012; Misaelides, 2011; Wang and Peng, 2010).

Some of the most relevant applications of natural zeolites in the clean-up of aqueous streams contaminated with heavy metals are summarized in Table 4.

Table 4. Application of natural zeolites for the clean-up of aqueous streams contaminated with heavy metals

Natural zeolite	Heavy metals	Initial concentration (mg/L)	Efficiency	Application	Reference
Clinoptilolite	Co ²⁺ , Cu ²⁺ , Zn ²⁺ , Mn ²⁺	100-400	66.1% (Cu ²⁺) 77.96% (Co ²⁺) 45.96% (Zn ²⁺) 19.84 (Mn ²⁺)	Industrial wastewater treatment	Erdem et al., 2004
Clinoptilolite and mordenite	Cu ²⁺ , Ni ²⁺ , Zn ²⁺	5-100		Metal finishing and electroplating wastewater	Cabrera et al., 2005
Kaolin and natural mordenite	Cr ²⁺	500	2.01 – 4.10 (mg Cr(III)/g)		Cavarribias et al., 2006
Clinoptilolite and chabazite	Pb ²⁺ , Cd ²⁺ , Cr ⁶⁺ , Zn ²⁺ , Cu ²⁺ , Ni ²⁺ , CO ²⁺			Effluents contaminated with mixed heavy metals	Ouki and Kavannagh, 1999
Clinoptilolite	Fe ³⁺ , Cu ²⁺ , Mn ²⁺ , Zn ²⁺	20-400	60-100	Treatment of and mine drainage	Motsi et al., 2009
Clinoptilolite	Pb ²⁺ , Cd ²⁺	0.044-1.779 (mmol L ⁻¹ Cd ²⁺) 0.024-1.448 (mmol L ⁻¹ Pb ²⁺)	0.6(nmol/g)		Berber-Mendoza et al., 2006
Clinoptilolite, gismondine, heulandite, offretite, quartz modified by chemical treatment	Cu ²⁺ , Ba ²⁺ , SO ₄ ²⁻		1.35 meq g ⁻¹ SO ₄ ²⁻ 0.97 meq g ⁻¹ isopropylxantlale ions		da Rosa Oliveira and Rubio, 2007
Clinoptilolite and mordenite	Cd ²⁺ , Pb ²⁺ , Cu ²⁺ , Zn ²⁺	10 ⁻⁶ – 10 ⁻³ M (10 ⁻³ Ca ²⁺ as a competing cation)	65 – 95% (Pb ²⁺) 15-25 (Cd ²⁺)		Yuan et al., 1999

Zeolite (not specified)	Cd^{2+}	1.50-5.20 $\text{mgCd}^{2+}/\text{L}$	95	Diminishing the toxicity generated by Cd^{2+} in aquatic media	James and Sampath, 1999
Clinoptilolite (Na-exchanged)	Various, in the presence of ammonium ions			Wastewater treatment	Blanchard et al., 1984
Natural zeolite (not specified)	Fe^{2+} , Pb^{2+} , Cd^{2+} , Zn^{2+}			Mining wastewater treatment	Wingenfelder et al., 2005
Natural and pretreated zeolites	Pb^{2+} , Cd^{2+}			Wastewater treatment	Curkovic et al., 1997
Clinoptilolite	Cr^{2+} , Cu^{2+} , Fe^{2+} , Mn^{2+} , Ni^{2+} , Pb^{2+} , Zn^{2+}			Sewage sludge composting	Zorpas et al., 2000
Clinoptilolite	Cu^{2+} , Cd^{2+} , Pb^{2+} , Zn^{2+} in the presence of ammonium			Pollutants removal from aqueous streams	Cincotti et al., 2001
Clinoptilolite (natural and treated)	Fe^{3+} , Cu^{2+} , Mn^{2+} , Zn^{2+}	20-400	$\text{Fe}^{3+} > \text{Zn}^{2+} > \text{Cu}^{2+} > \text{Mn}^{2+}$ 80-99	Acid mine drainage	Motsi et al., 2009
Clinoptilolite (50% content in natural zeolitic tuff)	Zn^{2+} , Cu^{2+} , Pb^{2+}	0.5 – 10 mmol L^{-1}	4-20 meqL^{-1}	Removal from aqueous solution	Peric et al., 2004
Clinoptilolite	Pb^{2+} , Cu^{2+} , Cd^{2+} , Cs^{2+} in single and ternary systems		93-98% (NaCl treated zeolite) 67-71% (NaOH treated zeolite) 33-46% untreated zeolite		Lee and Moon, 2001
Clinoptilolite	Cr^{3+} , Ni^{2+} , Zn^{2+} , Cu^{2+} , Cd^{2+}	10-200 mg/L		Purification of metal electroplating wastewater	Alvarez-Ayuso et al., 2003
Natural zeolite (not specified)	Hg^{2+}		1.21 meq/g sorbent	Purification of industrial effluents from cooper smelter and refinery	Chojnacki et al., 2004

5. Conclusions

The application of natural zeolites for environmental clean-up is increasing mainly due to their properties and significant worldwide occurrence. The heavy metal removal is attributed to different mechanisms, which consist mainly of adsorption and ion-exchange processes.

The experimental conditions such as temperature, pH, external surface activity, presence of hydrated dissolved species and their dimensions, existence of competing cations and other agents (complexing compounds) can affect the sorption efficiency. The majority of studies on the rate of heavy metals ions uptake by various categories of zeolites pointed out that the sorption process is commonly rapid and the maximum adsorption can be found in the first hours of contact.

The controlling mechanism of retention processes can be assessed by using several models: the pseudo-first-order kinetic model suggested by Lagergren for the sorption in solid/liquid systems, pseudo second-order kinetics, intraparticle diffusion kinetics etc.

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References

- Abraham R., (1993), *Dyes Environmental Chemistry*, In: *Encyclopaedia of Chemical Technology*, **8**, 672–783.
- Abusafa A., Yucel H., (2002), Removal of ^{137}Cs from aqueous solutions using different cationic forms of a natural zeolite: clinoptilolite, *Separation and Purification Technology*, **28**, 103–116.
- Abuzaid N.S., Nakhla G.F., (1996), Design and economic aspects of activated carbon adsorption in relation to the effect of dissolved oxygen, *Environmental Progress*, **15**, 128-134.
- Ackley M.W., Salil U. Rege S.U, Saxena H., (2003), Application of natural zeolites in the purification and separation of gases, *Microporous and Mesoporous Materials*, **61**, 25–42.
- Álvarez-Ayuso E., García-Sánchez A., Querol X., (2003), Purification of metal electroplating waste waters using zeolites, *Water Research*, **37**, 4855-4862.
- Apostol L.C., Gavrilescu M., (2009), Application of natural materials as sorbents for persistent organic pollutants,

- Environmental Engineering and Management Journal*, **7**, 301-308.
- Apostol L.C., Pereira L., Pereira R., Gavrilescu M., Alves M.M., (2012), Biological decolorization of xanthene dyes by anaerobic granular biomass, *Biodegradation*, DOI 10.1007/s10532-012-9548-7.
- Armagan B., Ozdemir O., Turan M., Celik M.S., (2003), The removal of reactive azo dyes by natural and modified zeolites, *Journal of Chemical Technology and Biotechnology*, **78**, 725-732.
- Barrer R.M., (1978), *Zeolites and Clay Minerals as Sorbents and Molecular Sieves*, Academic Press, FRS London.
- Bedioui F., (1995), Zeolite-encapsulated and clay-intercalated metal porphyrin, phthalocyanine and Schiff-base complexes as models for biomimetic oxidation catalysts: an overview, *Coordination Chemistry Reviews*, **144**, 9-68.
- Betianu C., Caliman F.A., Gavrilescu M., Cretescu I., Cojocaru C., Poullos I., (2008), Response surface methodology applied for Orange II photocatalytic degradation in TiO₂ aqueous suspensions, *Journal of Chemical Technology and Biotechnology*, **83**, 1454-1465.
- Berber-Mendoza M.S., Leyva-Ramos R., Alonso-Davila P., Mendoza-Barron J., Diaz-Flores P.E., (2006), Effect of pH and temperature on the ion-exchange isotherm of Cd(II) and Pb(II) on clinoptilolite, *Journal of Chemical Technology and Biotechnology*, **81**, 966-973.
- Blanchard G., Maunaye M., Martin G., (1984), Removal of heavy metals from waters by means of natural zeolites, *Water Research*, **18**, 1501-1507.
- Brinza L., Dring M. J., Gavrilescu M., (2007), Marine micro and macro algal species as biosorbents for heavy metals, *Environmental Engineering and Management Journal*, **6**, 237-251.
- Brinza L., Nygard C.A., Dring M.J., Gavrilescu M., Benning L.G., (2009), Cadmium tolerance and adsorption by the marine brown alga *Fucus vesiculosus* from the Irish Sea and the Bothnian Sea, *Bioresource Technology*, **100**, 1727-1733.
- Bosso S.T., Enzweiler J., (2002), Evaluation of heavy metal removal from aqueous solution onto scolecite, *Water Research*, **36**, 4795-4800.
- Cabrera C., Gabaldon C., Marzal P., (2005), Sorption characteristics of heavy metal ions by a natural zeolite, *Journal of Chemical Technology and Biotechnology*, **80**, 477-481.
- Caliman F.A., Gavrilescu M., (2008), Sorption of cationic dyes from aqueous solution onto natural clay. Equilibrium and kinetic study, *Environmental Engineering and Management Journal*, **7**, 301-308.
- Caliman F.A., Curteanu S., Betianu C., Gavrilescu M., Poullos L., (2008), Neural networks and genetic algorithms optimization of the photocatalytic degradation of Alcian Blue 8GX, *Journal of Advanced Oxidation Technologies*, **11**, 316-326.
- Caliman F.A., Gavrilescu M., (2009), Pharmaceuticals, personal care products and endocrine disrupting agents in the environment - a review, *CLEAN-Soil, Air, Water*, **37**, 277-303.
- Caliman F.A., Robu B.M., Smaranda C., Pavel V.L., Gavrilescu M., (2011), Soil and groundwater cleanup: benefits and limits of emerging technologies, *Clean Technologies and Environmental Policy*, **13**, 241-268.
- Caputo D., Pepe F., (2007), Experiments and data processing of ion exchange equilibria involving Italian natural zeolites: a review, *Microporous and Mesoporous Materials*, **105**, 222-231.
- Castaldi P., Santona L., Enzo S., Melis P., (2008), Sorption processes and XRD analysis of a natural zeolite exchanged with Pb²⁺, Cd²⁺ and Zn²⁺ cations, *Journal of Hazardous Materials*, **156**, 428-434.
- Chojnacki A., Chojnacka K., Hoffmann J., Górecki H., (2004), The application of natural zeolites for mercury removal: from laboratory tests to industrial scale, *Minerals Engineering*, **17**, 933-937.
- Cincotti A., Lai N., Orru R., Cao G., (2001), Sardinian natural clinoptilolites for heavy metals and ammonium removal: experimental and modeling, *Chemical Engineering Journal*, **84**, 275-282.
- Kocaoba S., Orhan Y., Akyüz T., (2007), Kinetics and equilibrium studies of heavy metal ions removal by use of natural zeolite, *Desalination*, **214**, 1-10.
- Colella C., (1999), Natural zeolites in environmentally friendly processes and applications, *Studies in Surface Science and Catalysis*, **125**, 641-655.
- Cooney D.O., (1999), *Adsorption Design for Wastewater Treatment*, Lewis Publishers, Boca Raton.
- Covarrubias C., Garcia R., Arriagada R., Yanez J., Garland M.T., (2006), Cr(III) exchange on zeolites obtained from kaolin and natural mordenite, *Microporous and Mesoporous Materials*, **88**, 220-231.
- Crini G., (2006), Non-conventional low-cost adsorbents for dye removal: a review, *Bioresource Technology*, **97**, 1061-1085.
- Curkovic L., Cerjan-Stefanovic S., Filipan T., (1997), Metal ion exchange by natural and modified zeolites, *Water Research*, **31**, 1379-1382.
- da Rosa Oliveira C., Rubio J., (2007), Adsorption of ions onto treated natural zeolite, *Materials Research*, **10**, 407-412.
- Diale P.P., Mkhize S.S.L., Muzenda E., Zimba J., (2011), The sequestration of heavy metals contaminating the wonderfonteinspruit catchment area using natural zeolite, *World Academy of Science, Engineering and Technology*, **74**, 766-772.
- Do D.D., (1998), *Absorption Analysis: Equilibria and Kinetic*, Imperial College Press, London.
- Doula M., Ioannou A., Dimirkou A., (2002), Copper adsorption and Si, Al, Ca, Mg, and Na release from clinoptilolite, *Journal of Colloid and Interface Science*, **245**, 237-250.
- Dyer A., Abdel Gawad A.S., Mikhail M., Enamy H., Afshang M., (1991), The natural zeolite, laumontite, as a potential material for the treatment of aqueous nuclear wastes, *Journal of Radioanalytical and Nuclear Chemistry Letters*, **154**, 265-276.
- Dwyer J., Parish R.V., (1983), Infrared and thermal studies of the interaction of transition-metal ions with the framework of type-X zeolites, *Inorganica Chimica Acta*, **75**, 229-234.
- EC, (2001), Pollutants in urban waste water and sewage sludge, Report prepared by I. C. Consultants Ltd London, Technical University Munich, IRSA Rome, ECA Barcelona for Directorate General Environment, Thornton I. (coordinator), Office for Official Publications of the European Communities, Luxembourg, On line at: http://ec.europa.eu/environment/waste/sludge/pdf/sludge_pollutants.pdf
- Eligwe C.A., Okolue N.B., Nwambu C.O., Nwoko C.I.A., (1999), Adsorption thermodynamics and kinetics of Mercury (II), Cadmium (II) and Lead (II) on lignite, *Chemical Engineering and Technology*, **22**, 45-49.

- Englert A.H., Rubio J., (2005), Characterization and environmental application of a Chilean natural zeolite, *International Journal of Mineral Processing*, **75**, 21-29.
- Erdem E., Karapinar N., Donat R., (2004), The removal of heavy metal cations by natural zeolites, *Journal of Colloid and Interface Science*, **280**, 309-314.
- Filippidis A.A., (2010), Environmental, industrial and agricultural applications of Hellenic Natural Zeolite, *Hellenic Journal of Geosciences*, vol. 45, 91-100
- Flanigen E.M., (1980), *Molecular Sieve Zeolite Technology-The First Twenty-Five Years*, In: *Proceedings of the 5th International Conference on Zeolites*, Rees L.V.C. (Ed.) Heyden, London, 760-780.
- Gavrilescu M., Macoveanu M., (1999), Process engineering in biological aerobic waste-water treatment, *Acta Biotechnologica*, **19**, 111-145.
- Gavrilescu M., Macoveanu M., (2000), Attached-growth process engineering in wastewater treatment, *Bioprocess Engineering*, **23**, 95-106.
- Gavrilescu M., (2004), Removal of heavy metals from the environment by biosorption, *Engineering in Life Science*, **4**, 219-232.
- Gavrilescu M., (2005), Fate of pesticides in the environment and its bioremediation, *Engineering in Life Science*, **5**, 497-526.
- Gavrilescu M., Teodosiu C., Gavrilesu G., Lupu L.M., (2008), Strategies and practices for sustainable use of water in industrial papermaking processes, *Engineering in Life Sciences*, **8**, 99-124.
- Gavrilescu M., (2009), Behaviour of persistent pollutants and risks associated with their presence in the environment - Integrated studies, *Environmental Engineering and Management Journal*, **8**, 1517-1531.
- Gupta V.K., Carrott P.J.M., Ribeiro Carrott M.M.L., Suhas, (2009), Low-cost adsorbents: growing approach to wastewater treatment—a review, *Critical Reviews in Environmental Science and Technology*, **39**, 783-842.
- Han R., Zhang J., Han P., Wang Y., Zhao Z., Tang M., (2009), Study of equilibrium, kinetic and thermodynamic parameters about methylene blue adsorption onto natural zeolite, *Chemical Engineering Journal*, **145**, 496-504.
- Hartmann M., Kullmann S. Keller H., (2010), Wastewater treatment with heterogeneous Fenton-type catalysts based on porous materials, *Journal of Materials Chemistry*, **20**, 9002-9017.
- Hendricks N.R., (2005), The application of high capacity ion exchange adsorbent material, synthesized from fly ash and acid mine drainage, for the removal of heavy and trace metals from secondary co-disposed process waters, PhD Thesis, University of Western Cape, South Africa.
- Henschel D.B., (1998), Cost analysis of activated carbon versus photocatalytic oxidation for removing organic compounds from indoor air, *Journal of the Air & Waste Management Association*, **48**, 985-994.
- Hlihor R.M., Gavrilesu M., (2009), Removal of some environmentally relevant heavy metals using low-cost natural sorbents, *Environmental Engineering and Management Journal*, **8**, 353-372.
- Hlihor R.M., Apostol L.C., Smaranda C., Pavel L.V., Căliman F.A., Robu B.M., Gavrilesu M., (2009), Bioavailability processes for contaminants in soils and their use in risk assessment, *Environmental Engineering and Management Journal*, **8**, 1199-1206.
- Inglezakis V.J., Loizidou M.D., Grigoropoulou H.P., (2001), Applicability of simplified models for the estimation of ion exchange diffusion coefficients in zeolites, *Journal of Colloid Interface Science*, **234**, 434-441.
- Inglezakis V.J., Hadjiandreou K.J., Loizidou M.D., Grigoropoulou H.P., (2001), Pretreatment of natural clinoptilolite in a laboratory-scale ion exchange packed bed, *Water Research*, **35**, 2161-2166.
- James R., Sampath K., (1999), Effect of zeolite on the reduction of cadmium toxicity in water and a freshwater fish, *Oreochromis mossambicus*, *Bulletin of Environmental Contamination and Toxicology*, **62**, 222-229.
- Jorgensen T.C., Weatherley L.R., (2003), Ammonia removal from wastewaters by ion exchange in the presence of organic contaminants, *Water Research*, **37**, 1723-1728.
- Jovic-Jovicic N., Milutinovic-Nikolic A., Grzetic I., Jovanovic D., (2008), Organobentonite as efficient textile dye sorbent, *Chemical Engineering and Technology*, **31**, 567-574.
- Judd S., Judd C., (2011), *The MBR Book: Principles and Applications of Membrane Bioreactors for Water and Wastewater Treatment*, Elsevier.
- Kayabali K., Kezer H., (1998), Testing the ability of bentonite-amended natural zeolite (clinoptilolite) to remove heavy metals from liquid waste, *Environmental Geology*, **34**, 95-102.
- Kocaoba S., Orhan Y., Tanil Akyüz T., (2007), Kinetics and equilibrium studies of heavy metal ions removal by use of natural zeolite, *Desalination*, **214**, 1-10.
- Krasner S.W., Westerhoff P., Chen B., Rittmann B.E. Seong-Nam Nam S.-N., Amy G., (2009), Impact of wastewater treatment processes on organic carbon, organic nitrogen, and DBP precursors in effluent organic matter, *Environmental Science and Technology*, **43**, 2911-2918.
- Kragovic M., Dakovic A., Sekulic Z., Trgo M., Ugrina M., Peric J., Gatta C.D., (2012), Removal of lead from aqueous solutions by using the natural and Fe(III)-modified zeolite, *Applied Surface Science*, **258**, 3667-3673.
- Kulkarni A.A., Deshpande M., Pandit A.B., (2000), Techniques of wastewater treatment. 2. Future technologies, *Resonance*, **5**, 64-74.
- Lai T., Cao A., Zucca A., Carucci A., (2012), Use of natural zeolites charged with ammonium or carbon dioxide in phytoremediation of lead- and zinc-contaminated soils, *Journal of Chemical Technology and Biotechnology*, DOI 10.1002/jctb.3788.
- Lee Y., von Gunten U., (2010), Oxidative transformation of micropollutants during municipal wastewater treatment: Comparison of kinetic aspects of selective (chlorine, chlorine dioxide, ferrate^{VI}, and ozone) and non-selective oxidants (hydroxyl radical), *Water Research*, **44**, 555-566.
- Lee D.H., Moon H., (2001), Adsorption equilibrium of heavy metals on natural zeolites, *Korean Journal of Chemical Engineering*, **18**, 247-256.
- Leinonen H., Lehto J., (2001), Purification of metal finishing waste water with zeolites and activated carbons, *Waste Management and Research*, **19**, 45-57.
- Li Z., Burt T., Bowman R.S., (2000), Sorption of ionizable organic solutes by surfactant-modified zeolite, *Environmental Science and Technology*, **34**, 3756-3760.
- Lim S.J., Park W., Kim T.-H., Shin I.H., (2012), Swine wastewater treatment using a unique sequence of ionexchange membranes and bioelectrochemical

- system, *Bioresource Technology*, <http://dx.doi.org/10.1016/j.biortech.2012.05.021>.
- Liu Z.-h., Kanjo Y., Mizutani S., (2009), Removal mechanisms for endocrine disrupting compounds (EDCs) in wastewater treatment — physical means, biodegradation, and chemical advanced oxidation: A review, *Science of the Total Environment*, **407**, 731–748.
- Markovska L.T., Vera D. Meshko V.D., Marinkovski M.S., (2006), Modeling of the adsorption kinetics of zinc onto granular activated carbon and natural zeolite, *Journal of the Serbian Chemical Society*, **71**, 957–967.
- Misaelides P., F. Macásek, T.J. Pinnavaia, C. Colella, (1999), *Natural Microporous Materials in Environmental Technology*, Vol. 362 of NATO science series. Series E. Applied sciences, Springer.
- Misaelides P., (2011), Application of natural zeolites in environmental remediation: A short review, *Microporous and Mesoporous Materials*, **144**, 15–18.
- Mondale K.D., Carland R.M., Aplan F.F., (1995), The comparative ion exchange capacities of natural sedimentary and synthetic zeolites, *Minerals Engineering*, **8**, 535–548.
- Mortier W.J., Structure Commission of the International Zeolite Association, (1982), *Compilation of Extra Framework Sites in Zeolites*, Butterworth Scientific Ltd.
- Motsi T., (2010), Remediation of acid mine drainage using natural zeolite, PhD Thesis, School of Chemical Engineering, The University of Birmingham, United Kingdom.
- Motsi T., Rowson N.A., Simmons M.J.H., (2009), Adsorption of heavy metals from acid mine drainage by natural zeolite, *International Journal of Mineral Processing*, **92**, 42–48.
- Motsi T., Rowson N.A., Simmons M.J.H., (2011), Kinetic studies of the removal of heavy metals from acid mine drainage by natural zeolite, *International Journal of Mineral Processing*, **101**, 42–49.
- Muga H.E., Mihelcic J.R., (2008), Sustainability of wastewater treatment technologies, *Journal of Environmental Management*, **88**, 437–447.
- Mulligan C.N., Yong R.N., Gibbs B.F., (2001), Remediation technologies for metal-contaminated soils and groundwater: an evaluation, *Engineering Geology*, **60**, 193–207.
- Mumpton F.A., (1983), *Zeo-Agriculture: Use of Natural Zeolites in Agriculture and Aquaculture*, Westview Press, Boulder, CO.
- Mumpton F.A., (1999), La roca magica: Uses of natural zeolites in agriculture and industry, *Proceedings of the National Academy of Sciences of the United States of America*, **96**, 3463–3470.
- Nguyen M.L., Tanner C.C., (1998), Ammonium removal from wastewaters using natural New Zealand zeolites, *New Zealand Journal of Agricultural Research*, **41**, 427–446.
- Otero M., Rozada F., Moran A., Calvo L.F., Garcia A.I., (2009), Removal of heavy metals from aqueous solution by sewage sludge based sorbents: competitive effects, *Desalination*, **239**, 46–57.
- Ouki S.K., Kavannagh M. (1999), Treatment of metals-contaminated wastewaters by use of natural zeolites, *Water Science and Technology*, **39**, 115–122.
- Ozaydin S., Kocer G., Hepbasli A., (2006), Natural zeolites in energy applications, *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, **28**, 1425–1431.
- Pagga U., Brown D., (1986), The degradation of dye-stuffs: Part II Behaviour of dyestuffs in aerobic biodegradation tests, *Chemosphere*, **15**, 479–491.
- Panayotova M.I., (2001), Kinetics and thermodynamics of copper ions removal from wastewater by use of zeolite, *Waste Management*, **21**, 671–676.
- Pansini M., (1996), Natural zeolites as cation exchangers for environmental protection, *Mineralium Deposita*, **31**, 563–575.
- Panswad T., Luangdilok W. (2000), Decolorization of reactive dyes with different molecular structures under different environmental conditions, *Water Research*, **34**, 4177–4184.
- Papelis C., Roberts P.V., Leckie J.O., (1995), Modeling the rate of cadmium and selenite adsorption on microporous and mesoporous transition aluminas, *Environmental Science and Technology*, **29**, 1099–1108.
- Pavelic K., Hadzija M., Bedrica L., Pavelic J., Dikic I., Katic M., Kralj M., Herak Bosnar M., Kapitanovic S., Poljak-Blazi M., Krizanac S., Stojkovic R., Jurin M., Subotic B., Colic M., (2001), Natural zeolite clinoptilolite: new adjuvant in anticancer therapy, *Journal of Molecular Medicine*, **78**, 708–720.
- Perić J., Trgo M., Vukojević Medvidović N., (2004), Removal of zinc, copper and lead by natural zeolite—a comparison of adsorption isotherms, *Water Research*, **38**, 1893–1899.
- Pitcher S.K., Slade R.C.T., Ward N.I., (2004), Heavy metal removal from motorway stormwater using zeolites, *Science of the Total Environment*, **334–335**, 161–166.
- Ramallo R.S., (1977), *Introduction to Wastewater Treatment Processes*, Academic Press, New York.
- Randall W.B., Boardman G.D., Dietrich A.M., Michelsen D.L., Padaki M., (1993), Pilot scale study on anaerobic treatment of textile wastewaters, hazardous and industrial wastes, In: *Proceedings of the Mid Atlantic Industrial Waste Conference*, Webber S. (Ed.), CRC Press, 218–227.
- Richardson, J.F., Harker, J.H., (2002), *Coulson & Richardson's Chemical Engineering*, Vol 2, Fifth ed., Butterworth Heinemann.
- Rizzo L., Meric S., Guida M., Kassinos D., Belgiorno V., (2009), Heterogenous photocatalytic degradation kinetics and detoxification of an urban wastewater treatment plant effluent contaminated with pharmaceuticals, *Water Research*, **43**, 4070–4078.
- Robinson T., McMullan G., Marchant R., Nigam P., (2001), Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative, *Bioresource Technology*, **77**, 247–255.
- Robu B.M., Caliman F.A., Betianu C., Gavrilescu M., (2007), Methods and procedures for environmental risk assessment, *Environmental Engineering and Management Journal*, **6**, 573–592.
- Rozendal R.A., Hamelers H.V.M., Rabaey K., Keller J., Buisman C.J.N., (2008), Towards practical implementation of bioelectrochemical wastewater treatment, *Trends in Biotechnology*, **26**, 450–459.
- Rozic M., Cerjan-Stefanovic S., Kurajica S., Vancina V., Hodzic E., (2000), Ammoniacal nitrogen removal from water by treatment with clays and zeolites, *Water Research*, **34**, 3675–3681.
- Shepherd A., (2001), Activated carbon adsorption for treatment of VOC emissions, Presented at the 13th Annual EnviroExpo, Boston Massachusetts, May 2001.

- Smaranda C., Gavrilesu M., Bulgariu D., (2011), Studies on sorption of Congo red from aqueous solution onto soil, *International Journal of Environmental Research*, **5**, 177-188.
- Tchobanoglous G., Burton F.L., Metcalf & Eddy, Stensel H.D., (2004), *Wastewater Engineering: Treatment and Reuse*, McGraw Hill.
- Tschernich R.W., (1992), *Zeolites of the World*, Geoscience Press, Phoenix.
- Trgo M., (2009), Natural zeolites as multifunctional environmental friendly materials their application for removal of Pb and Zn from binary solutions, Paper presented at *2nd Slovenian-Croatian Symposium on Zeolites*, Ljubljana, 2009.
- Vaca Mier M., Lopez Callejas R., Gehr R., Jimenez Ciseros B.E., Alvarez P.J.J., (2001), Heavy metal removal with Mexican clinoptilolite: multicomponent ionic exchange, *Water Research*, **35**, 373-378.
- von Sperling M., (2007), *Biological Wastewater Treatment, vol. 1: Wastewater Characteristics, Treatment and Disposal*, IWA Publishing, London.
- Wang S., Ariyanto S., (2007), Competitive adsorption of malachite green and Pb ions on natural zeolite, *Journal of Colloid and Interface Science*, **314**, 25-31.
- Wang S., Peng Y., (2010), Natural zeolites as effective adsorbents in water and wastewater treatment, *Chemical Engineering Journal*, **156**, 11-24.
- Wang S., Zhu Z.H., (2006), Characterization and environmental application of an Australian natural zeolite for basic dye removal from aqueous solution, *Journal of Hazardous Materials*, **136**, 946-952.
- Widiastuti N., Wu H., Ang M., Dong-ke Zhang D.-k., (2008), The potential application of natural zeolite for greywater treatment, *Desalination*, **218**, 271-280.
- Wingenfelder U., Hansen C., Furrer G., Schulin R., (2005), Removal of heavy metals from mine waters by natural zeolites, *Environmental Science and Technology*, **39**, 4606-4613.
- Woinarski A.Z., Stevens G.W., Snape I., (2006), a natural zeolite permeable reactive barrier to treat heavy-metal contaminated waters in Antarctica. Kinetic and fixed-bed studies, *Transactions of Institution of Chemical Engineers, Part B*, **84**, 109-116.
- Xu W., Li L.Y., Grace J.R., (2010), Zinc removal from acid rock drainage by clinoptilolite in a slurry bubble column, *Applied Clay Science*, **50**, 158-163.
- Yuan G., Seyama H., Soma M., Theng B.K.G., Tanaka A., (1999), Adsorption of some heavy metals by natural zeolites : XPS and batch studies, *Journal of Environmental Science and Health, Part A: Toxic/Hazardous Substances and Environmental Engineering*, **34**, 625-648.
- Zorpas A.A., Constantinides T., Vlyssides A.G., Haralambous I., Loizidou M., (2000), Heavy metal uptake by natural zeolite and metals partitioning in sewage sludge compost, *Bioresource Technology*, **72**, 113-119.