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CHARACTERIZATION AND APPLICATION OF CLINOPTILOLITE FOR REMOVAL OF HEAVY METAL IONS FROM WATER RESOURCES

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Abstract: The aim of this article is characterization of natural zeolite (clinoptilolite) and its application for removal of heavy metals from aqueous solution. Characterization of the natural zeolite from Beli Plast deposit, Kardjali, was conducted using: classical chemical analysis, XRD, SEM/EDS, DTA/TG/DTG, XRF, FTIR and BET. Based on the results of the chemical composition, XRD, SEM/EDS and FTIR analyses, it is evident that the major component of the working material (~ 95%) is clinoptilolite. In fact, the working material is alumino-silicate with high silicate module and it is of clinoptilolite type. The applied material has the specific surface area of 31.3 m^2/g determined by BET method with nitrogen adsorption. The maximum capacity of clinoptilolite towards zinc, nickel and cobalt removal under the studied conditions is approximately 3.5 mg/g, for copper and manganese is approximately 4.5 mg/g and for lead ions is approximately 30 mg/g. Natural zeolite (clinoptilolite) was used as a potential raw material for the purpose of removal of Cu(II), Zn(II), Mn(II), Pb(II), Co(II) and Ni(II) ions from model solutions. The experimental results were obtained in a laboratory scale batch glass reactor with continuous stirring at 400 rpm. The adsorption of studied heavy metal ions from solution were efficiently onto used adsorbent and approximately 90% from ions were removed from single ion solutions. Generally, it can be concluded that studied clinoptilolite is a potential raw material for effective removal of heavy metals ions from various types of waste waters.

Key words: clinoptilolite; natural zeolite; heavy metals; characterization

1. INTRODUCTION

Zeolites are crystalline minerals that are broadly distributed in nature. During the millions of years, the layers of volcanic ash underwent some physical and chemical changes on exposure to high temperatures and pressures, which resulted in the formation of a diverse group of zeolites.

Zeolites are crystalline aluminosilicates with open 3D framework structures built of SiO_4 and AlO_4 tetrahedra linked to each other by sharing all the oxygen atoms to form regular intracrystalline cavities and channels of molecular dimensions. Zeolite frameworks are made up of four coordinated atoms forming tetrahedra, which are linked by their corners. This feature makes a rich variety of beautiful structures of zeolite. The framework structure of zeolite contains channels, cages, and cavities. These are linked and big enough to allow easy drift of the resident ions and molecules into and out of the structure. Zeolite's low specific density is the result of the system of large voids, which are interconnected and form long wide channels of various sizes depending on the compound (Peskov, 2015). This ability puts zeolites in the class of materials known as "molecular sieves".

Zeolites are very useful minerals. They have been used in various industries recently. This is due to their many attractive characteristics. There are three main uses of zeolites in industry: catalysis, adsorption, and ion exchange.

Application of zeolites in waste water treatment is very important. The properties that make natural zeolite an attractive alternative for the treatment of waste water are as follows: They are cheap since they are relatively abundant (Cui et al., 2006). They have a favorable cation exchange capacity (CEC) (Yuan et al., 1999). They have good selectivity for cations (Malliou et al., 1994). Zeolites have a high surface area due to their porous and rigid structure (Alvarez-Ayuso et al., 2003). They also act as molecular sieves, and this property can easily be modified to increase the performance of the zeolite (Sprynskyy et al., 2006). In acidic conditions, the zeolites have good structural stability and can be regenerated easily. The acidic solutions can be neutralized by zeolite, which is achieved through the exchange of H^+ ions from solution with the cations in the zeolite structure (Leinonen et al., 2001).

Because of these features, zeolites have been a growing interest in the adsorption of heavy metals from solution. Many researchers have shown the feasibility of using natural zeolite in the adsorption of heavy metals under different experimental conditions such as temperature, pH, concentration, and agitation speed (Erdem et al., 2004; Motsi, 2010; Cincotti et al., 2006).

The Balkan Peninsula is rich with natural zeolites. In this paper the zeolite, type clinoptilolite from the Beli Plast deposit, Kardjali, is studied. It is studied from several authors. About the geology of Eastern Rhodopes Mountains, Bulgaria, where Beli Plast deposite is located, writes Yanev (Yanev et al., 2006). Dimova studies in detail the structural changes that take place in clinoptilolite, when undergoing greater Zn^{2+} exchange at higher temperatures and durations (Dimova et al., 2008). Taneva in her study determined the optimal parameters of ion-exchange of ammonium ions and sorption of phosphate ions using activated and modified Bulgarian clinoptilolite (Taneva, 2012). Popov et al. (2012) characterized natural zeolites in their study and made comparison of the Bulgarian deposits Belia Bair and Beli Plast with zeolite from Northern Chile. Markovska studied determination of the order of selective adsorption of heavy metals by natural clinoptilolite and synthetic zeolite type L (Markovska et al., 2017).

In this study besides the characterization of natural zeolite (clinoptilolite) from the Beli Plast deposit, Kardjali, the application for removal of heavy metals (Cu(II), Zn(II), Mn(II), Pb(II), Co(II) and Ni(II) ions) from aqueous solution is also studied. Characterization of the natural zeolite was conducted using: classical chemical analysis, XRD, SEM /EDS, DTA/TG/DTG, XRF, FTIR and BET. The maximum capacity of the clinoptilolite was determined through Langmuir and Freundlich adsorption isotherm models.

2. BRIEF GEOLOGY OF BELI PLAST DEPOSIT

During the Paleogene, after the Mesozoic-Cenozoic subduction leading to the closure of the Tethys Ocean, microplates of African origin collided with the southern edge of the Eurasian plate (Ricou, 1994). Significant collision-related magmatism (Yanev and Bahneva, 1980; Yanev et al., 1998) occurred on the southern edge of the Eurasian plate and resulted in formation of many volcanic areas extending from the Alps to northwestern Turkey. One of them is Eastern Rhodopes (southern Bulgaria) where ca. 7000 km^2 are now covered by volcanic rocks. The Eastern Rhodopes volcanic association (37 to 25 Ma, Lilov et al., 1987) is bimodal andesite-latitic (1ocally up to basaltic) and rhyolitic in composition. Intermediate and acid varieties are present in almost equal volumes. The acid volcanic glass, deposited in marine environment, was transformed into zeolites, mainly clinoptilolite, less mordenite and analcime, accompanied by clay minerals, opal-CT and adularia (Yanev et al., 2004). In the top of the pyroclastic sections in some places non-zeolitized glass is still preserved. After the discovery of the zeolitized tuffs (Aleksiev, 1968) an impressive amount of work on the Eastern Rhodopes zeolitized pyroclastic rocks dealing with zeolite mineralogy (Kirov, l974; Djourova, 1976) and features of some zeolite deposits (Aleksiev and Djourova, 1982, Djourova and Aleksiev, 1990, and references therein; Raynov et al., 1997; Ivanova et al., 2001) has been published.

Several intermediate and acid volcanic phases alternating in time have been distinguished (Ivanov, 1963; Yanev et al., 1998). The first two of them (acid and intermediate) are Priabonian, all the others are Rupelian, named 1s, 2nd, 3rd and 4th Early Oligocene phases, respectively. In the Late Oligocene, this volcanic activity was followed by dyke intrusion. Here is given brief description of the products of the acid phases because only the acid glass is zeolitized (Figure 1). Bentonitized latitic beds separate the pyroclastics of the acid phases.

Beli Plast, Gorna Krepost, Most and Golobradovo belong to the 1st Early Oligocene phase of volcanism, Belia Bair, Zhelezna Vrata and the uppermost parts of the Gorna Krepost – to the 2nd phase (Yanev et al., 2004). The mordenite deposit Liaskovetz belongs to the 1st phase. Actually in exploitation are Beli Plast and Zhelezna Vrata. The quantity of the zeolitized material in these deposits varies between some tens to some hundreds of millions of tons. The results of the geological research are summarized in Raynov et al., (1997) and references therein.

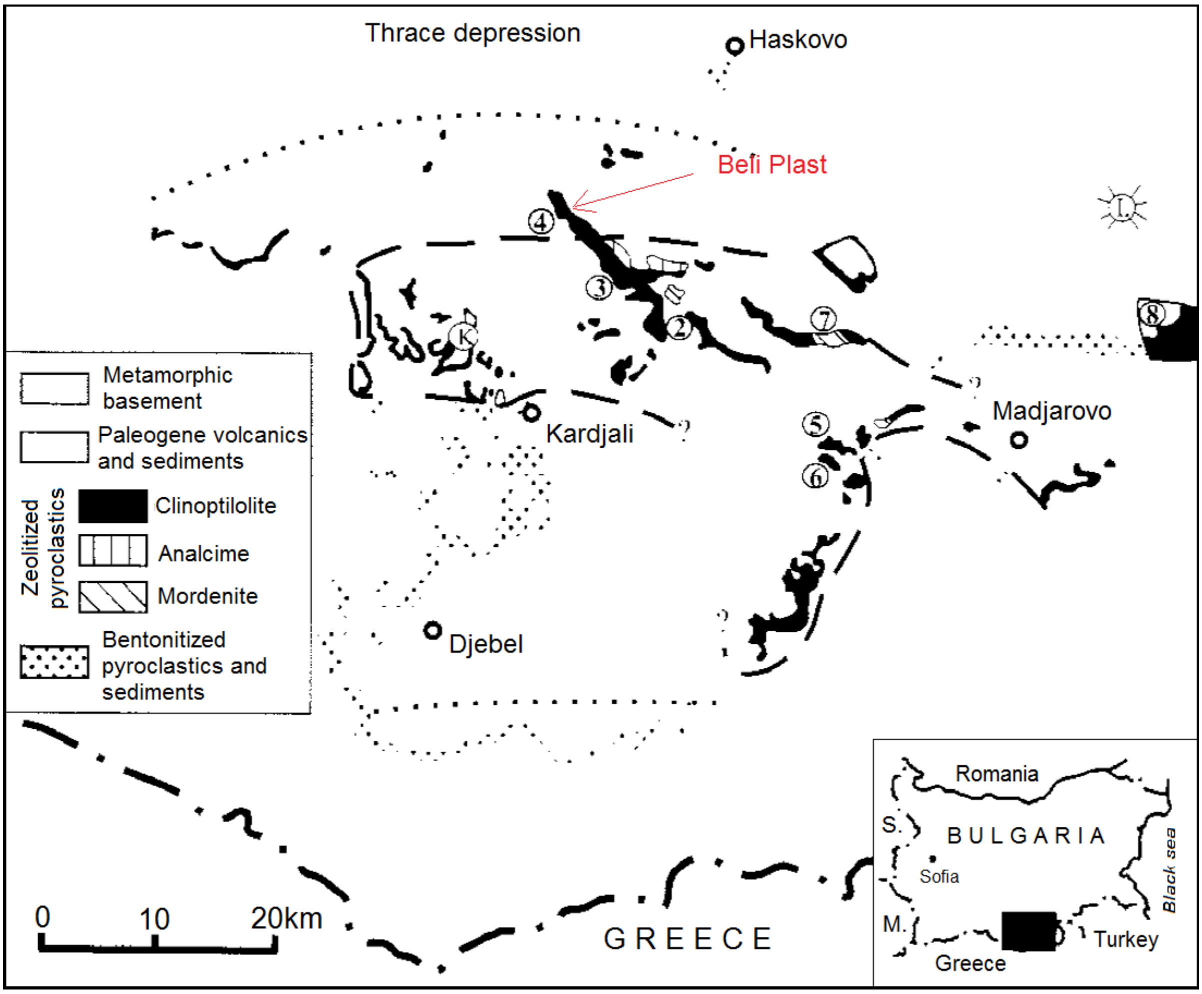

Fig. 1. Distribution of acid pyroclastic rocks from proxymal volcanic phases (First Early Oligocene acid phase) in the Eastern Rhodopes (modified from the Geological Map of Bulgaria 1:100 000), their alteration products (zeolites and clay rninerals) and deposits; dashed line indicates limit of distribution of the pyroclastic flows+fall-out tuffs: dotted Iine indicates limit of distribution of the fall-out tuffs only . Numbers indicate: clinoptilolite deposits – 2. Most; 3. Gorna Krepost; 4. Beli Plast; 5. Golobradovo; 6. Moriantzi; 7. Liaskovetz mordenite deposit, 8. Sheinovetz caldera (clinoptilolite+mordenite)

3. MATERIAL AND METHODS

The natural zeolite (clinoptilolite) from the Beli Plast deposit in the Eastern Rhodopes region, Kardjali, Bulgaria, is used for the research.

Particle characterization reveals information on the physical and chemical nature of zeolite particles, which is related to its ability to remove heavy metal ions from solution. Characterization of the natural zeolite was conducted using several advanced analyses.

3.1. *Analytical methods*

A classical silicate chemical analysis has been applied for determination of the chemical composition of the raw material and particle size distribution was define using sieve analysis.

X-Ray Diffractometer 6100 from Shimadzu was used to investigate the mineralogical structure of natural zeolite samples. The surface morphology of natural zeolite was studied using a scanning electron microscope, VEGA3 LMU. This particular microscope is also fitted with an Inca 250 EDS system, Energy Dispersive Spectroscopy. Thermal analysis of the natural zeolite (clinoptilolite) is carried out in an inert stream of nitrogen with a heating rate of 10°/min using the DTA analyzer. XRF analyses were performed using XRF ARL 9900 XP. FTIR spectra for the structural analyses were recorded using the KBr pellets in the wavelength range of 500–4000 cm^{-1} with Perkin-Elmer Spectrum 100.

Specific surface area of clinoptilolite was determined by BET method using Micrometrics

TriStar II 3020 with adsorption of nitrogen. The determination of CEC followed the Standard Test Method for Methylene Blue Index of Zeolite, according to the ASTM C 837 – 81.

3.2. *Experimental procedure and conditions*

Adsorptions of heavy metals ions (Cu(II), Zn(II), Mn(II) and Pb(II)) on natural zeolite (clinoptilolite) were performed with synthetic single component ion solutions of Cu(II), Zn(II), Mn(II) and Pb(II) ions with different initial concentration (5, 25, 50, 200 and 400 mg/l). Synthetic single compo-nent solutions of these metals were prepared by dissolving a weighed mass of the analytical grade salt $CuSO_4{\cdot}5H_2O$, $ZnSO_4{\cdot}7H_2O$, $MnSO_4{\cdot}H_2O$ and $Pb(NO_3)_2$, appropriately, in 1000 ml distilled water. Initial pH value 3.5 of prepared solutions was adjusted by adding 2% sulfuric acid and controlled by 210 Microprocessor pH Meter. The experiments were performed in a batch mode in a series of beakers equipped with magnetic stirrers by contacting a mass of 5 g adsorbent with a volume of solution, 100 ml. Adsorbent and aqueous phase were suspended by magnetic stirrer at 400 rpm. The agitation time was varied up to 360 minutes. All experiments were performed at room temperature on $20 \pm 1^{\circ}C$. The initial and remaining concentrations of metal ions were determined by ICP-AES Agilent (Zendelska et al., 2015; Zendelska et al., 2015; Golomeova et al., 2016).

Adsorptions of heavy metals ions Co(II) and Ni(II) on natural zeolite, clinoptilolite, were performed with model solutions of $Co(NO_3)_2$ with different initial Co(II) concentration (350–650 μg/l) and $Ni(NO_3)_2$ with different initial Ni(II) concentration (350–650 μg/l). The agitation at 400 rpm was varied up to 300 minutes at room temperature on $22 \pm 1^{\circ}C$. The experiments were done in volume of solution of 200 ml, at pH value 6 and 0.5 g mass of adsorbent (Jakupi, 2016).

The adsorption capacity was calculated using the following expression:

$$q_{\mathrm{e}} = \frac{V(C_0 - C_e)}{m}\ \text{(mg/g)}, \tag{1}$$

where: q_{e} is the mass of adsorbed metal ions per unit mass of adsorbent (mg/g), C_0 and C_e are the initial and final metal ion concentrations (mg/l), respectively, V is the volume of the aqueous phase (l) and m is the mass of adsorbent used (g).

Degree of adsorption, in percentage, is calculated as:

$$\mathrm{AD\%} = \left(1 - \frac{C_e}{C_0}\right) \cdot 100. \tag{2}$$

3.3. *Equilibrium studies*

Equilibrium studies generally involve the determination of the adsorption capacity of a given material. This determination is important in accessing the potential of the material as an economic and commercially viable adsorber.

Experimental data were also fitted to conventional adsorption mathematical models, namely the Freundlich and Langmuir models. These were used to predict the adsorption performance of clinoptilolite. The Langmuir isotherm model (Langmuir, 1918), based on monolayer coverage of adsorbent surfaces by the adsorbate at specific homogeneous sites within the adsorbent, is represented as:

$$q_{\mathrm{e}} = \frac{q_m K_l C_e}{1 + K_l C_e}, \tag{3}$$

where q_{e} (mg/g) is the amount of solute adsorbed per unit mass of adsorbent at equilibrium; C_e (mg/l), is the residual adsorbate concentration in solution at equilibrium; q_m (mg/g) is the amount of solute adsorbed per unit mass of adsorbent corresponding to complete coverage of available sites, K_l (l/mg), is the Langmuir adsorption coefficient, this constant is related to the affinity between the adsorbent and solute which is evaluated through linearization of Equation 3:

$$\frac{1}{q_{\mathrm{e}}} = \frac{1}{k_l q_m C_e} + \frac{1}{q_m}. \tag{4}$$

The Freundlich isotherm model, based on monolayer adsorption on heterogeneous surfaces with a non-uniform distribution of adsorption heat, is represented as:

$$q_{\mathrm{e}} = k_f C_e^{1/n}, \tag{5}$$

where k_f and n are empirical Freundlich constants that are dependent on experimental conditions. k_f (mg/g) is an indicator of adsorption capacity, while n (g/l) is related to the adsorption intensity or binding strength. Their values were determined from the linear form of the Freundlich equation, given by:

$$\log q_{\mathrm{e}} = \log k_f + \frac{1}{n} \log C_e, \tag{6}$$

where $1/n$ is the heterogeneity factor; values of $1/n$ << 1 indicate heterogeneous adsorbents, while values closer to or even 1 indicate a material with relatively homogeneous binding sites (Papageorgiou, 2006).

4. RESULTS AND DISCUSSION

4.1. *Characteristics of clinoptilolite*

4.1.1. *Classical chemical analysis*

Particle characterization reveals information on the physical and chemical nature of natural zeolite particles, which is related to its ability to remove heavy metal ions from solution.

Table 1

Chemical composition and physicochemical characteristics of zeolite samples

Physical properties			
Density	hydrated	2.16 g/cm^3	
	dehydrated	1.88 g/cm^3	
Thermal dehydration		Up to 500°C	
Damp		max 10%	
Pore volume		0.34 cm^3 H_2O/cm^3 crystal	
Chemical properties			
Typical chemical composition in % wt			
SiO_2	69.68	CaO	2.01
Al_2O_3	11.40	Na_2O	0.62
TiO_2	0.15	K_2O	2.90
Fe_2O_3	0.93	H_2O	13.24
MgO	0.87	P_2O_5	0.02
MnO	0.08	ratio Si/Al	4.0–5.2
Total cation exchange capacity		1.8–2.2 meq/g	

The natural zeolite from Kardali, Republic of Bulgaria, was used in a recent study.

The general characteristics of used natural zeolite, such as chemical composition, physical characteristics and cation exchange capacity are presented in Table 1. The particle size range of the natural zeolite used in this study was 0.8–2.5 mm.

4.1.2. *XRD analysis*

This technique is based on observing the scattering intensity of an X-ray beam hitting a sample as a function of incident and scattered angle, polarization, and wavelength or energy. The diffraction data obtained are compared to the database maintained by the International Centre for Diffraction Data, in order to identify the material in the solid samples. Measurements are performed at an interval of 2θ angle from 0 to 80°. XRD diffractogram shows that in the range of 2θ angle of 20–25° an intense peak appears at the angle of 22° which is characteristic for the natural zeolite (clinoptilolite). Other clearly expressed intensive reflexes point of the crystal structure of a strictly defined crystal lattice characteristic for clinoptilolite. In fact these reflexes show tetrahedral structure of zeolite, characteristic for its canals and cavities. The results of XRD (Figure 2) showed that the natural zeolite contained clinoptilolite in the majority and quartz in minority.

Popov (Popov et al., 2012) studied clinoptilolite from the Beli Plast deposit and shows that their sample is with 82% clinoptilolite obtained by semiquantitative X-ray diffraction analysis on a D-500 Siemens diffractometer.

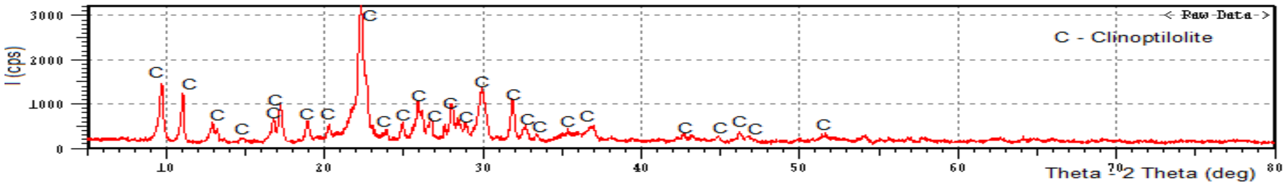

Fig. 2. X–ray diffraction of natural zeolite

4.1.3. *SEM/EDS*

Micrographs of natural zeolite samples obtained from SEM analysis are given in Figure 3. The micrographs clearly show a number of macro-pores in the zeolite structure. The micrographs also show well defined crystals of clinoptilolite.

An electron beam was directed onto different parts of the samples in order to get a more accurate analysis (Figure 4) and the elemental composition of natural zeolite (clinoptilolite) is presented in Table 2.

Results of EDS analysis showed that the predominant exchangeable cations in natural zeolite (clinoptilolite) structure were K^+ and Ca^{2+}. The same can be confirmed from the chemical analysis (Table 1). Popov et al. (2012) in their study show that the predominant exchangeable cations in zeolite from thye Beli Plast deposit are Ca-K-Na.

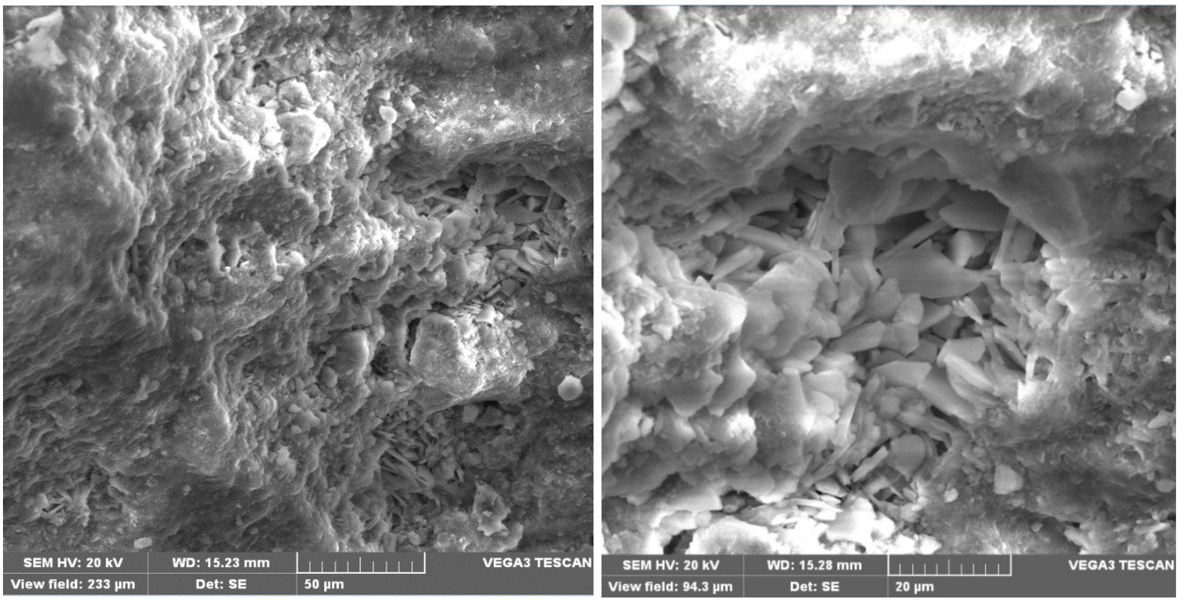

Fig. 3. Micrographs of natural zeolite samples obtained from SEM analysis

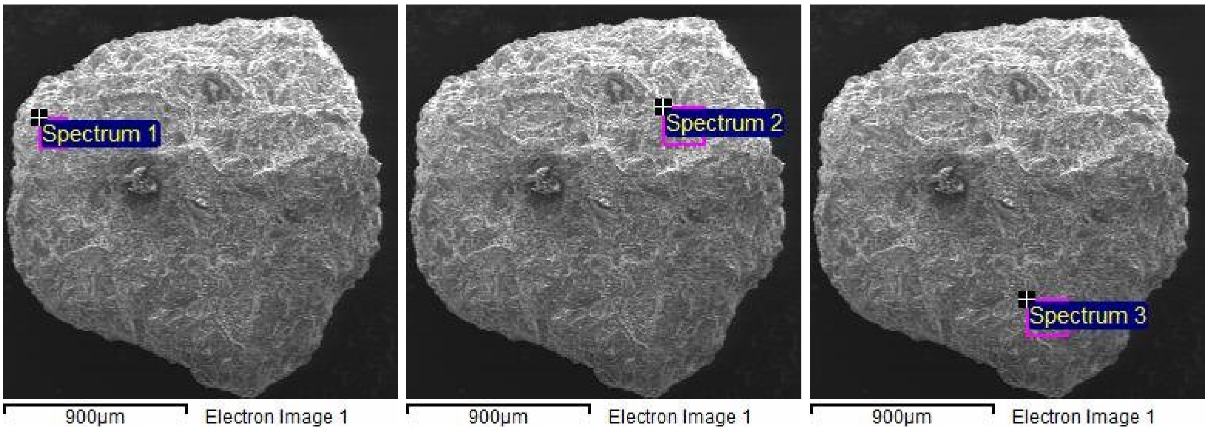

Fig. 4. EDS analysis showing the scanning method for natural zeolite

Table 2

EDS analysis showing the elemental composition of natural zeolite

Element	Spect 1	Spect 2	Spect 3	Average	Std. deviation
O	58.46	55.4	58.83	57.56	1.882
Na	0.27	0.15	0.3	0.24	0.079
Mg	0.72	0.66	0.77	0.72	0.055
Al	5.28	5.52	5.03	5.28	0.245
Si	29.55	31.36	29.47	30.13	1.068
K	2.73	2.96	2.44	2.71	0.26
Ca	1.9	2.42	1.66	1.99	0.388
Fe	1.1	1.53	1.5	1.38	0.24
Total	100	100	100	100	

4.1.4. *Thermal analysis*

DTA, TG and DTG analyses of natural zeolite (clinoptilolite) are presented in Figure 5.

The conducted thermal analyses show the occurrence of endothermic effects, typical for natural zeolite, that do not cause structural changes, and these curves are result of the thermal dehydration wherein the investigated natural zeolite loosens physically and chemically bound water. DTG curve in Figure 5 shows intense peak at temperature of 100°C, resulting from the beginning of the thermal dehydration.

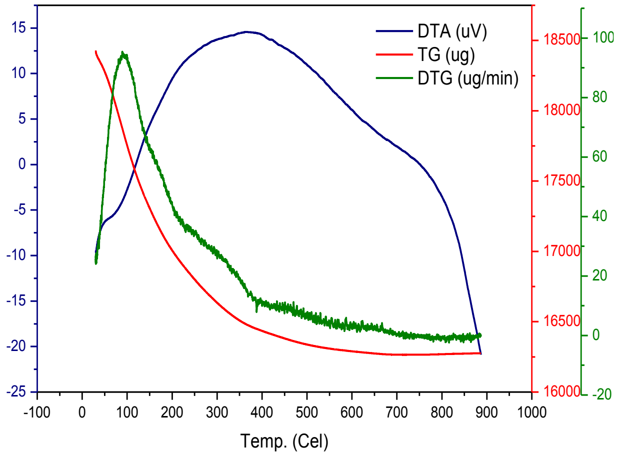

Fig. 5. DTA, TG, DTG of natural zeolite (clinoptilolite)

In order to define the maximum level of thermal dehydration of the investigated material, the TG curve of the clinoptilolite is shown in Figure 5 as well. The curve, which is exponentially decreasing function, suggests that the maximum thermal dehydration occurs at the temperature range of 450–500°C, after which the system enters the steady state. Based on this TG curve, the loss of ignition is determined and is from 12.94 to 13.24% mass. Based on these studies, the further working conditions for quantitative XRF analysis are defined.

4.1.5. *XRF analysis*

In order to determine the quantitative presence of the oxides in the working material, natural zeolite (clinoptilolite), XRF (X-ray fluorescence) analysis was conducted. The results of quantitative composition are given in Table 3.

The results listed in the Table 3 confirmed that this is a highly silicate natural porous material, with abundance of SiO_2, 67.83% mass. The ratio SiO/Al_2O_3 is 6/1 which shows that the major component of the material ~95% is clinoptilolite. The loss on ignition is 12.94% mass. and is due to the presence of chemically bound water in the channels and cavities of the tetrahedral structure of zeolite. The analyses were performed by igniting the sample at 950°C for 1h. This temperature was selected based on the results of the conducted thermal analysis.

Table 3

Composition of the clinoptilolite obtained by XRF analysis

Components	SiO_2	Al_2O_3	CaO	MgO	Fe_2O_3	Na_2O	TiO_2	SrO	Mn_2O_3	K_2O	ZnO	LOI
% mass	67.827	11.466	3.024	0.767	0.727	0.474	0.125	0.057	0.056	0.045	0.010	12.94

4.1.6. *FTIR analysis*

FTIR spectrum of clinoptilolite is shown in Figure 6. Analyzing the FTIR spectra, following can be concluded: intense band that occurs in the range of 3400–3500 cm^{-1} results from vibration of OH-groups of the present water. Band that appears in the range of 1600–1650 cm^{-1} is a result of molecularly bound water in the structure (deformation vibration). The vibration bands at 950–1250 cm^{-1} result from the structural units of the alumino-silicate lattice Si (Al)-O of the zeolite. Based on this structural analysis it is confirmed that this is a nanoporous alumino-silicate material with defined crystal structure and the presence of free and chemically bound water.

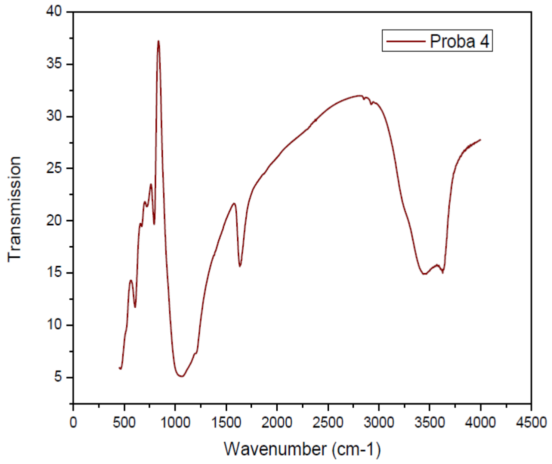

Fig. 6. FTIR spectrum of natural zeolite (clinoptilolite)

4.1.7. *BET method*

The specific surface area of natural zeolite (clinoptilolite) is determined by the amount of adsorbed nitrogen depending on the partial pressure. Based on the results obtained by the adsorption/desorption of nitrogen as a working gas, the specific surface area of the used natural zeolite was defined in one point and the specific area determined using the BET method (Table 4).

Based on the graphical dependence shown in Figure 7 it can be concluded that increasing the partial pressure of nitrogen increases its absorbed amount until all active centers, channels and cavities that are characteristic for the structure of this nanoporous material, are filled.

Figure 8 shows a linear form of the used BET method for determination of the specific surface area (m^2/g).

Table 4

Determination of the specific surface area of the natural zeolite (clinoptilolite)

Mass of the sample	0.0889 g
Degassing temperature	77.300 K
Specific surface area in one point	29.2609 m^2/g
BET specific surface area	31.2854 m^2/g

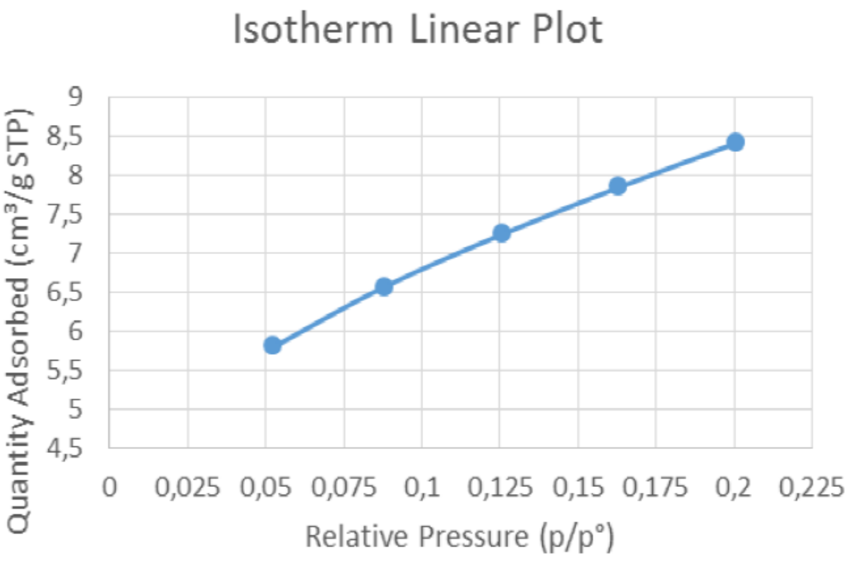

Fig. 7. Dependence of the amount of adsorbed nitrogen from the partial pressure at natural zeolite (clinoptilolite)

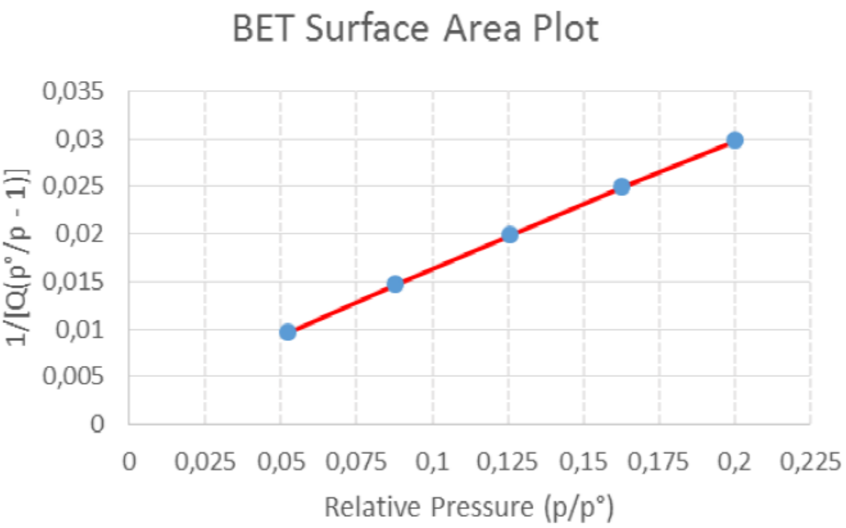

Fig. 8. Graphical determination of the specific surface area of natural zeolite (clinoptilolite) using BET method

4.2. *Equilibrium studies*

The main objective of the equilibrium studies was to determine the maximum capacity of clinoptilolite towards copper, zinc, manganese, lead, nickel and cobalt removal under the studied conditions. The data obtained from equilibrium experiments were fitted to the Langmuir and Freundlich adsorption isotherms. The values of the constants in the models and correlation coefficients obtained are summarized in Table 5.

Table 5

Calculated equilibrium adsorption isotherm constants for the uptake of metals from solution by clinoptilolite

Heavy metal	Experimental		Langmuir				Freundlich			
	q_e (mg/g)	C_e (mg/l)	q_m (mg/g)	K_l (l/mg)	R^2	R_L	K_f (l/mg)	1/n	N (g/l)	R^2
Cu	4.6880	166.60	5.2690	0.0404	0.9243	0.0583	0.3566	0.5247	1.9059	0.7135
Zn	3.6392	218.04	3.7272	0.0968	0.9900	0.0250	0.3934	0.4545	2.2002	0.9111
Mn	4.0596	197.02	4.2680	0.0382	0.9252	0.0614	0.2625	0.5339	1.8730	0.8282
Pb	30.140	21.21	37.590	0.1726	0.8853	0.0143	1.1628	0.6803	1.4699	0.8346
Co	3.4000	0.1700	3.4597	0.1962	0.9984	/	/	/	/	/
Ni	3.3800	0.2000	3.6870	0.0411	0.9995	/	/	/	/	/

According to the Freundlich model, values of the heterogeneity factor 1/*n*, for all these metals, indicate that clinoptilolite is heterogeneous adsorbent. Natural zeolite should be a heterogeneous adsorbent due to its porous nature. Based on the correlation coefficients (R^2), the adsorption isotherms for these metals can be better described by the Langmuir model than Freundlich model. The applicability of the Langmuir isotherm suggests monolayer coverage of the metal ions at the surface of the clinoptilolite or that similar exchangeable ions with equivalent concentration were exchanged by metal ions. The R_L values reported in Table 5, show that the behaviour of metal ions adsorption for all studied metals was favourable ($0 < R_L < 1$).

The maximum capacity of clinoptilolite towards zinc, nickel and cobalt removal under the studied conditions is approximately 3.5 mg/g, for copper and manganese is approximately 4.5 mg/g and for lead ions is approximately 30 mg/g.

The difference in adsorption capacity of the natural zeolite for the heavy metal ions may be due to a number of factors which include hydration radii, hydration enthalpies and solubility of the cations. The hydration radii of the cations are: $r_H Mn^{2+} = 4.38$ Å, $r_H Zn^{2+} = 4.30$ Å, $r_H Co^{2+} = 4.23$ Å, $r_H Cu^{2+} = 4.19$ Å, $r_H Ni^{2+} = 4.04$ Å and $r_H Pb^{2+} = 4.01$ Å (Nightingale, 1959; Mobasherpour et al., 2012). The smallest cations should ideally be adsorbed faster and in larger quantities compared to the larger cations, since the smaller cations can pass through the micropores and channels of the zeolite structure with ease (Erdem et al., 2004). According to the hydration radii, the order of adsorption should be $Pb^{2+} > Ni^{2+} > Cu^{2+} > Co^{2+} > Zn^{2+} > Mn^{2+}$.

In this case, lead ions is with the highest maximum capacity and it is the first in the selectivity series. This is expected because lead ions is with the smallest hydration radius comparison with other studied ions. According to Markovska et al. (2017) the selectivity towards studied heavy metal cations (for 10 minutes) can be ordered as follows: $Fe^{2+} > Zn^{2+} > Mn^{2}+ > Pb^{2+} > Cd^{2}+ > Ni^{2+} > Cu^{2+}$. The difference in the selectivity of clinoptilolite may be due to different experimental conditions.

4.3. *Application of clinoptilolite*

Application of zeolites in waste water treatment for removal of heavy metals is very important. In this paper the results of application of natural zeolite, clinoptilolite from Kardjali are presented. Experimental results of the adsorption of heavy metal cations from aqueous solutions onto natural zeolite (clinoptilolite) are shown in Table 6.

The adsorptions of studied heavy metal ions from solutions were efficiently onto used adsorbent and approximately 90% from ions were removed from single ion solutions.

Table 6

Application of clinoptilolite for heavy metals removal

Heavy metal ions	Conditions	Percentage adsorbed (%)
Cu(II)	T = 20 ± 1°C pH 3.5 m = 5 g adsorbent C_0 = 5 mg/l agitation speed = 400 rpm	97.840
Zn(II)		94.00
Mn(II)		89.60
Pb(II)		97.60
Co(II)	T = 22 ± 1°C pH 6 m = 0.5 g adsorbent C_0 = 450 µg/l agitation speed = 400 rpm	98.80
Ni(II)		88.88

C_0 – initial metal concentration

In terms of the examined conditions, copper, zinc, lead and manganese ions are with higher initial concentration according to the acid waste water from mines, and initial concentration for cobalt and nickel ions are above the maximum permissible limits for surface waste water from the process industry. Generally, it can be concluded that investigated clinoptilolite is a potential raw material for effective removal of heavy metals ions from various types of waste waters.

5. CONCLUSION

Based on the results of the chemical composition, XRD, SEM/EDS and FTIR analyses it is evident that the major component of the working material is clinoptilolite, approximately 95%. In fact, the working material is alumino-silicate with high silicate module and it is of clinoptilolite type.

The applied clinoptilolite has the specific surface area of 31.3 m^2/g determined by BET method with nitrogen adsorption. The obtained maximum capacity of clinoptilolite using Langmuir and Freundlich adsorption isoterms for removal of lead ions is 30 mg/g, approximately 4.5 mg/g for copper and manganese ions, and approximately 3.5 mg/g for zinc, nickel and cobalt ions.

The adsorptions of studied heavy metal ions from solution were efficiently onto used adsorbent and approximately 90% from ions were removed from single ion solutions. Generally, it can be concluded that investigated clinoptilolite is a potential raw material for effective removal of heavy metals ions from various types of waste waters.

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Резиме

КАРАКТЕРИЗАЦИЈА НА КЛИНОПТИЛОЛИТ И НЕГОВА ПРИМЕНА ЗА ОТСТРАНУВАЊЕ НА ЈОНИ НА ТЕШКИ МЕТАЛИ ОД ВОДНИ РЕСУРСИ

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Клучни зборови: клиноптилолит; природен зеолит; тешки метали; карактеризација

Целта на овој труд е карактеризација на природниот зеолит (клиноптилолит) и неговата примена за отстранување на тешки метали од водни раствори. Карактеризацијата на природниот зеолит од наоѓалиштето Бели Пласт, Карџали, е направена со: класични хемиски анализи, XRD, SEM/EDS, DTA/TG/DTG, XRF, FTIR и методот BET. Врз основа на резултатите од хемискиот состав и анализите, XRD, SEM/EDS и FTIR е констатирано дека станува збор за алумосиликатен материјал чија главна компонента е клиноптилолит со учество од околу 95%. Со методот BET со азотна атсорпција е одредена специфичната површина на материјалот која изнесува 31,3 m^2/g. Во рамките на испитувањето е одреден максимален капацитет на клиноптилолитот кој за отстранување на јоните на цинк, никел и кобал изнесува приближно 3,5 mg/g, за бакар и манган околу 4,5 mg/g и за јоните на олово околу 30 mg/g. Природниот зеолит беше употребен како потенцијална природна суровина за отстранување на јоните на Cu(II), Zn(II), Mn(II), Pb(II), Co(II) и Ni(II) од примероците на водни раствори. Експериментите се вршени во стаклени чаши со континуирано движење од 400 rpm. Резултатите од испитувањата покажаа дека атсорпцијата на наведените тешки метали од раствор со користење на наведениот апсорбент е ефикасна, при што е постигнато нивно отстранување од околу 90 %. Според тоа , може да се заклучи дека испитуваниот клиноптилолит може да се користи како потенцијална природна суровина за ефикасно отстранување на јони на тешки метали од загадени води.