

CHARACTERIZATION OF NATURAL ZEOLITE (CLINOPTILOLITE) AS ONE OF THE HIGH CATION EXCHANGE CAPACITY GEOPOLYMER MATERIAL

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Abstract

The aim of this research is to subject one of the specific and locally used natural zeolite (clinoptilolite) from Vranjska Banja, Serbia with high cation exchange capacity. Mineralogical - X-Ray Diffraction Analysis (XRD), Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) and determination of cation exchange capacity (CEC) were investigated. Results showed homogenous structure with dominant clinoptilolite - heulandite type zeolites as most abundant minerals. The important aspect of this research is possibility of wider usage of natural zeolite-clinoptilolite due to cost-efficiency aspects of this natural material that can be exploited in large amount from several Serbian deposits e.g. "Zlatokop" (Vranjska Banja) and "Igros Vidojević" (Brus), Serbia. The present of higher, but also extremely concentration of heavy metals in Pannonian, Internal Dinarides and wider European region lead us to boost novel high performance but economically viable techniques. The starting points are geochemical characterization of novel geo- materials before further water-treatment implementation.

Introduction

Natural zeolites are hydrated aluminosilicate minerals with valuable physicochemical properties, such as cation exchange, molecular sieving, catalysis and sorption. In the past decades, natural zeolites have found a variety of applications in adsorption, catalysis, building industry, agriculture, soil remediation, and energy. The use of natural zeolites for environmental applications is gaining new research interests mainly due to their properties and significant worldwide occurrence. Natural zeolite have also been reported for removal of anions and organics from water systems [1, 2, 3]. These materials are abundant and low-cost resources and have been found in many areas of the world. In this paper we will examine the characterization of zeolite (clinoptilolite) from the territory of the Republic Serbia.

The aim of this work is to determine the consistent, homogeneity and high CEC capacity for local and economically most affordable materials in order to be used in field investigations on groundwater and industrial wastewater most suitable purification/remediation material in order to recommend it for best available water treatment technology as main adsorbent.

The need for new geomaterial with high to superhigh cation exchange capacity (CEC) have been stated in many scientific papers and field investigations [1]. The aim of this study is to characterize zeolites from the investigated area of Serbia, in this case specific geochemical composition from natural zeolite (clinoptilolite) from Vranjska Banja, Serbia.

Experimental

The primary sample of zeolite, natural zeolite (clinoptilolite) from Vranjska Banja, Serbia ca. 1 kg, was prepared and dried by Standard methods for sample preparation (SRPS B.B8.080.) in Dryer - "Binder" (sample distributor Jones). The sample was analyzed for mineralogical - XRD analysis, SEM/EDS and determination of CEC. XRD and SEM analysis of the matrices were done in order to elucidate the microscopic structures and morphology of surfaces and CEC analysis will show specific content of exchangeable cations in clinoptilolite sample. Examination of the mineral composition of the sample was investigated by X-ray automatic powder diffractometer PHILIPS, model PW-1710. X-ray diffraction analysis was used to determine and monitor the phase composition of the sample. The intensities of diffracted CuK α X-rays radiation ($\lambda=1.54178\text{\AA}$) were measured at room temperature at intervals of $0.02^\circ 2\theta$ and a time of 1 s in the range from 4 to $65^\circ 2\theta$. The X-ray tube was loaded with a voltage of 40 kV and a current of 30 mA, while the slots for directing the primary and diffracted beam were 1° and 0.1 mm. Method for determination of exchangeable cations Ca^{2+} , Mg^{2+} , Na^+ and K^+ and cation exchange capacity was DM 10-0/40.

Results and discussion

The sample was examined by X - ray diffraction on a polycrystalline sample (powder). The diffractogram of the tested sample is presenting the clinoptilolite - heulandite type zeolites as most abundant minerals.

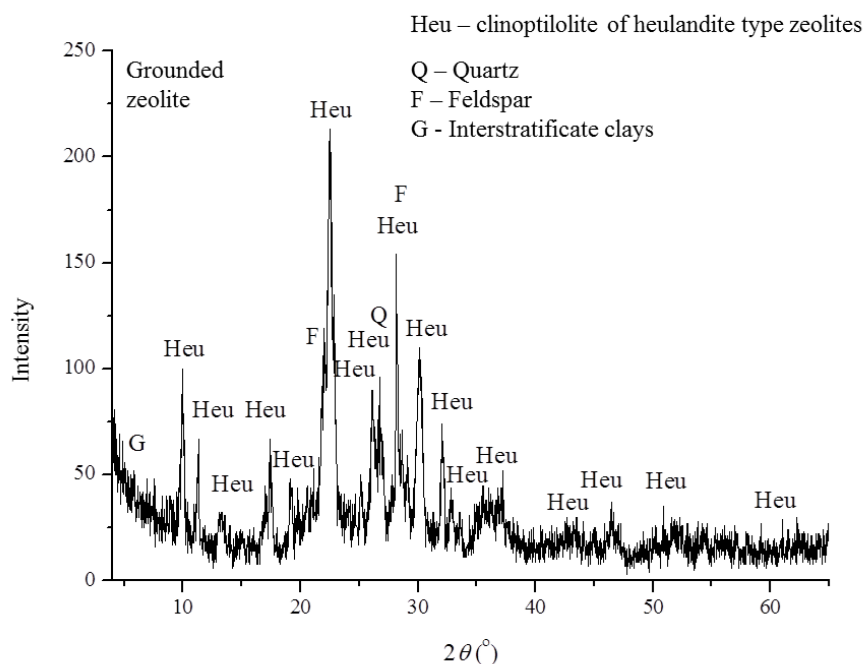


Figure 1. The diffractogram of the clinoptilolite (natural zeolites) from Vranjska Banja

The presence of the following minerals was determined in the analyzed sample: clinoptilolite-heulandite type zeolites, feldspar, quartz, interstratified clays, carbonates and mica. The most common minerals are zeolite and then feldspar, while quartz is significantly less common. Of the feldspar, plagioclase is predominantly represented, relative to K-feldspar. Semiquantitative share crystalline phases (minerals) is as follows: zeolites $\approx 85\%$, feldspars $\approx 10\%$, clays $\leq 5\%$, quartz 2-3%. Carbonates, respectively calcite and mica are present in the trace.

The next important targeted analysis of sample surfaces is Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) method and results can be seen from Figure 2. The SEM-micrograph shows from several to tens micrometers semi-homogenous structure and macro/meso-porosity. The brighter areas in the crystallites represent feldspar and darker areas clinoptilolite as in study from [4].

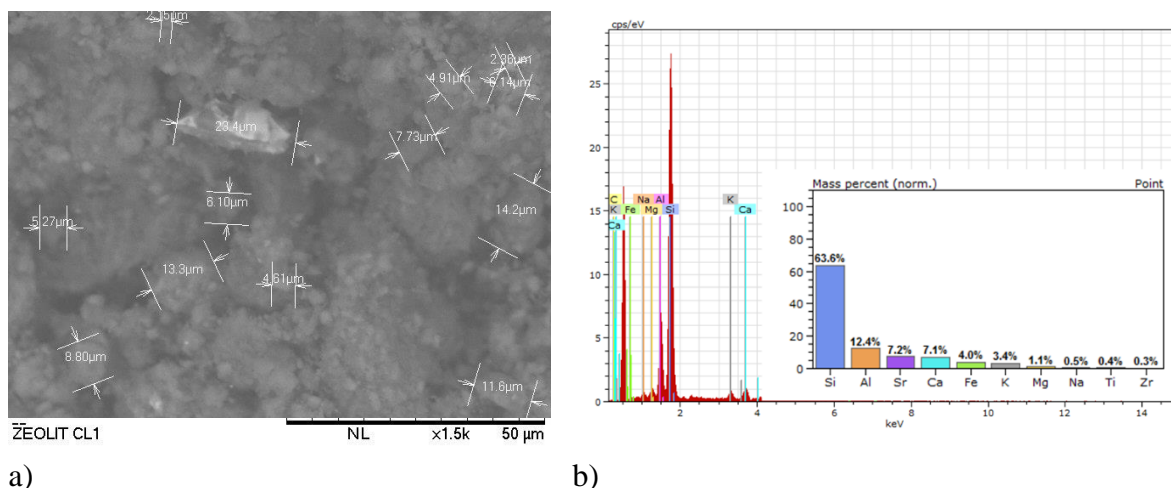


Figure 2. SEM-micrograph (a) and (b) EDS spectrum of the natural zeolite (clinoptilolite) sample

Generally, the important ratio for classification of zeolite from clinoptilolite type is Si/Al and according to the EDS analysis it was round 5.3 and accordingly higher than prescribed value of 4.5 [2] for this type. Additionally, previous studies support this examination with also similar Ca, Fe, K, Mg and Na content (Table 1) and similar chemical composition on globescale¹.

Table 1. Results of EDS analysis from natural zeolite (clinoptilolite) from Vranjska Banja, Serbia compared with other related zeolites (clinoptilolite) samples

Element	[norm. wt.%]	[norm. wt.%] ⁴	[norm. wt.%] ³
Silicon	69.98	65.63	70.90
Aluminium	13.19	12.97	12.40
Calcium	7.49	3.08	2.54
Iron	4.19	1.48	1.21
Potassium	3.57	1.33	4.46
Magnesium	1.12	1.41	0.83
Sodium	0.44	0.95	0.28
CEC (meq/g)	1.2	/	1.6–1.8

The results of determining the content of exchangeable cations are shown in Table 2:

Table 2. Results of determining the content of variable cations of zeolite samples (meq/100g)

Sample/ions		Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Σ _{cations}
Natural zeolite (clinoptilolite) from Vranjska Banja, Serbia		2,53	48,47	68,61	3,36	122,97

Due to many study observed in paper from Wang and Peng, 2008 the CEC value could clasify this zeolite as higher in the class with high potential for local but also comercial near region used as adsorbent with superhigh cation exchange capacity regarding previous [4,5] but also ongoing and future studies.

Conclusion

This research shows good potential and high CEC capacity of zeolite (clinoptilolite) from Vranjska Banja, Serbia. Future application will be based on this geochemical scanning of clinoptilolite as potentially well structure and geo-chemically powerful purification material.

Acknowledgements

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