

Characterization of raw and chemically activated natural zeolite as a potential sorbent for heavy metal ions from waste water

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In this study, raw and chemically activated natural zeolite from Zlatokop deposit (Serbia) were investigated by FTIR, XRD, SEM-EDX, TGA and BET in order to define their properties as further potential sorption materials. Obtained results indicate porous (meso-pore range) and defined crystal aluminosilicate structure of these materials, with Na⁺, K⁺, such as Ca²⁺ and Mg²⁺ as dominating exchangeable cations. Content of clinoptilolite (*ca.* 90%) indicates the high quality of the zeolite samples. Preliminary sorption analyses of these materials toward copper(II) ion from aqueous solution showed good removal efficiency for base activated zeolite (zVB_B) compared to raw natural (zVB_N) and acid activated (zVB_A) zeolite. Since these were preliminary sorption tests, the investigated zeolites will be further examined under different experimental conditions.

Key words: Zlatokop zeolite, activation, FTIR, XRD, SEM-EDX, TGA, BET, heavy metal sorption.

INTRODUCTION

Zeolites are crystalline aluminosilicate minerals with structures built of SiO₄ and AlO₄ tetrahedra which are linked by their corners. Natural zeolites are widely used: for purification of water, soil improvement, animal food production, food supplements and additives, radioprotection, etc. [1]. The possibilities of using zeolites for pollutants removal from wastewaters have been extensively studied. Their use is also stimulated by the availability and low cost, in addition to excellent physicochemical properties, like selective sorption of different metals and non-toxic nature [2, 3]. Also, zeolites have a high surface area due to their porous and rigid structure [4]. Clinoptilolite, a member of the heulandite group (HEU type zeolite), is the most abundant natural zeolite. Its tabular morphology shows an open reticular structure of easy access exhibited by (eight- and ten-membered ring) channels [5, 6].

The protection and improvement of water resources have received increased attention in the world. Over the years, various materials in native form or chemically modified, have been studied for their ability to remove pollutants from wastewaters. Studied materials should be low cost, widely available and environmentally friendly. [7]

In this study characterization of raw natural zeolite and chemically activated natural zeolite from Zlatokop deposit (Serbia) was done using FTIR, XRD, SEM-EDX, TGA and BET. These zeolites were investigated as a further potential

sorbent for inorganic (heavy metal ions, anions) and/or organic (industrial colours, pesticides, drugs) pollutants from water systems. Also, preliminary sorption analyses were done (waste water model system with Cu²⁺ ion). Raw natural nonactivated zeolite was designated further in the manuscript as „zVB_N“, while activated zeolites were designated as „zVB_A“ (acid activation – HCl) and „zVB_B“ (base activation – NaOH).

Zeolite deposit

Zlatokop deposit is located in south-east Serbia near Vranjska Banja and represents one of the largest zeolite deposits in Serbia (Figure 1a). This zeolite deposit is related to Miocene volcanic activity and classified as high-quality zeolite deposit in Serbia (more than 70% of clinoptilolite) [8] This deposit is related to volcanic and volcanic-clastic rocks of lake sediments, with estimated reserves of zeolite of *ca.* 0.59 Mt [9].

EXPERIMENTAL

Sample preparation and activation

Natural zeolite sample (Figure 1b) was crushed in an agate mortar and sieved in order to obtain fractions of different particle size. The fraction of 0.8 – 1.25 mm was washed with distilled water to remove surface dust and then dried in the oven at 100-105 °C. Prepared material was activated with 2M NaOH and 2M NaCl. The mixtures were stirred for 12 h using a magnetic stirrer at room temperature, separated by centrifugation, thoroughly washed with deionized water. The zeolite samples were dried in the oven at 100-105 °C.

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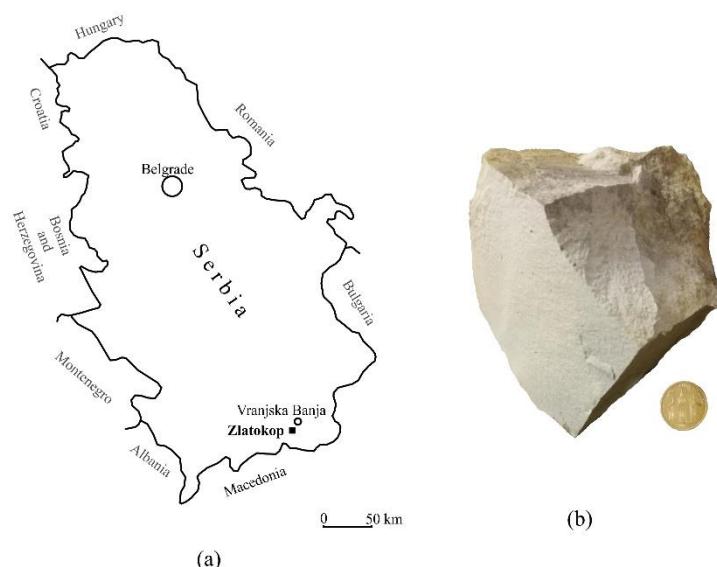


Figure 1. Geographical location of Zlatokop zeolite deposit (a) and zeolite sample (b)

Fourier transform infrared (FTIR) spectrometry

The FTIR spectra of samples were obtained by using KBr pellets with Fourier transform infrared spectrometer Bomem Hartmann & Braun MB-100 in the wavelength range $4000 - 400 \text{ cm}^{-1}$.

Scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX)

The morphology of the zeolite samples surface was analyzed by SEM (Hitachi SU8030). EDS analysis (Thermo Scientific NORAN System 7, USA) provided elemental information *via* the analysis of X-ray emissions from the sorbent surface. For SEM-EDX analysis samples were attached to aluminum stubs using Leit-C carbon cement. Samples were imaged uncoated.

Surface area analysis using the Brunauer-Emmett-Teller (BET) method

The specific surface area was measured by nitrogen adsorption using the Micromeritics Gemini 5 surface area analyzer, USA.

Thermogravimetric (TG) analysis

TG analysis was performed using TGA Q5000 (TA Instruments, USA).

X-ray diffraction (XRD) analysis

Zeolite samples were finely ground using a mortar and pestle and placed into standard sample holders. Data were collected with a Bruker D8 Advance X-ray Diffractometer (Bruker, Germany) in theta-theta geometry in reflection mode with $\text{Cu K}\alpha$ radiation. Data collection was between $5-70^\circ 2\theta$, step size of 0.02° and a counting time of 1 sec per step.

Preliminary sorption experiment

Preliminary sorption abilities of raw and chemically modified zeolites were investigated in a model system with copper(II) ion as we have done in our previous investigations. The concentrations of Cu(II) ions in the solution before and after adsorption were determined by using an atomic absorption spectrophotometer (AAAnalyst 300, Perkin Elmer, USA) [7, 10].

RESULTS AND DISCUSSION

FTIR. The FTIR spectra of zeolite samples recorded in the wavelength region between 400 and 4000 cm^{-1} are shown in Figure 2.

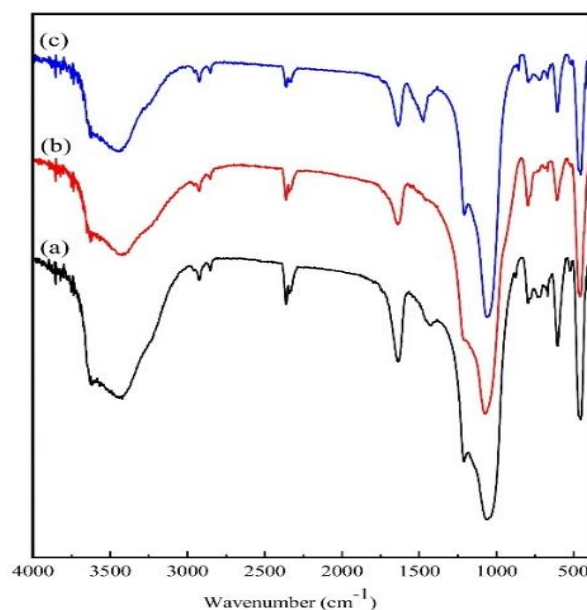


Figure 2. FTIR spectra of zVBN (a), zVBA (b) and zVBB (c).

Characteristic bands for natural zeolite can be identified. Wide band between 2900 and 3750 cm^{-1}

is attributed to the existence of OH group stretching vibrations (from Al-OH or present water). Deformation vibration of molecularly bound water in the zeolite structure is characterized by bands in the spectra in the region 1600-1650 cm^{-1} . The bands in the range 950-1250 cm^{-1} correspond to asymmetric stretching vibration of structural tetrahedra units of the aluminosilicate lattice Si(Al)-O of the zeolite. The bands in the range 455-790 cm^{-1} correspond to stretching vibration of O-Si(Al)-O groups and bending vibrations of Si(Al)-O bonds. According to the obtained data there are no significant changes in the FTIR spectra after chemical modification of natural zeolite, but it was confirmed that these are aluminosilicate materials with defined crystal structure [11, 12].

SEM-EDX. SEM micrographs of the investigated zeolite samples are presented on Figure 3. These micrographs show the porous and well-defined crystal structure of natural and modified zeolite samples.

EDX analysis was done by measuring different parts of the sample (seven points) in order to get more precise elemental compositions of the investigated samples (Figure 4).

Data from Figure 4 indicate the aluminosilicate structure of zeolite with Na^+ , K^+ , such as Mg^{2+} and Ca^{2+} as dominating exchangeable cations. Average values of these ions are decreasing after zeolite

activation with hydrochloric acid for Na^+ and K^+ by ca. 90%, while for Ca^{2+} and Mg^{2+} ions by ca. 55%. After base activation Na^+ value increases (ca. six times), K^+ and Ca^{2+} decrease (by ca. 20% and 10%, respectively), while there are no changes for Mg^{2+} value. All these changes are the result of ion exchange processes after acid and base modifications (H^+ or Na^+ or OH^- ions). These results are in accordance with literature data for zeolites from the Balkan region [13, 14].

XRD. XRD diffractograms of zVB_N , zVB_A and zVB_B samples are shown on Figure 5. According to the data from Figure 5 the dominant zeolite's mineral is clinoptilolite (ca. 90%), which confirms the appearance of an intense peak at the 2θ angle of 22° [15]. XRD data also showed that the investigated natural zeolite contains other minerals quartz, mordenite, albite and calcite in minority. Comparing XRD diffractograms of zVB_N , zVB_A and zVB_B it can be noticed that there are no significant differences between natural and chemically modified zeolites, except the disappearance of the calcite peak at the 2θ angle of around 29.5° [16] in the sample zVB_A , due to dissolving calcite in hydrochloric acid, which is in accordance with the EDX results where a decrease of carbon value by ca. 45% after acid and by ca. 20% after base activation can be noticed (Figure 4).

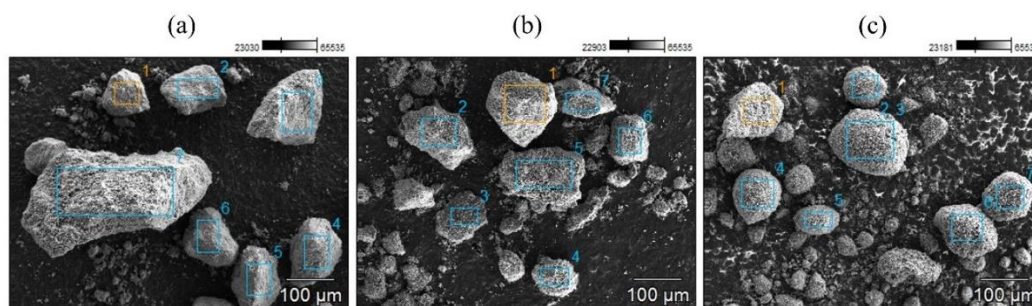


Figure 3. SEM micrographs of zVB_N (a), zVB_A (b) and zVB_B (c).

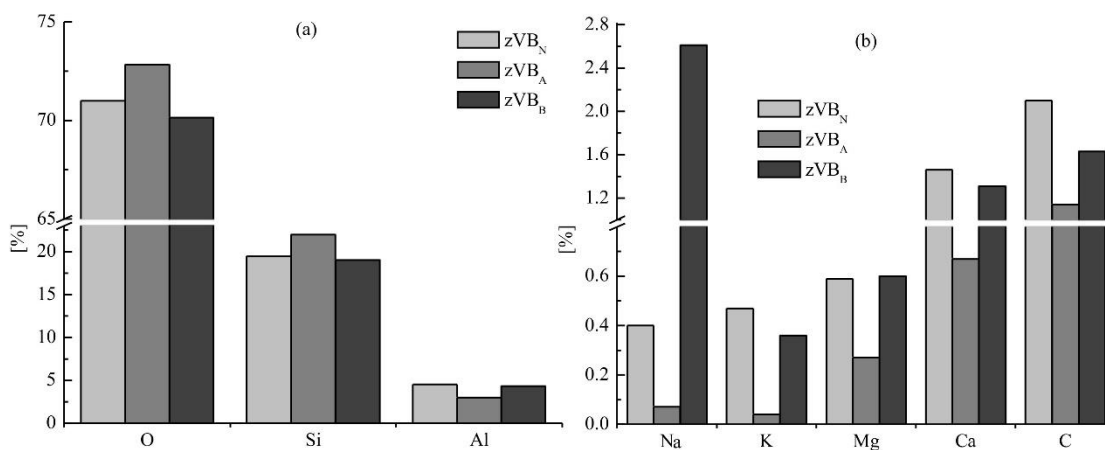


Figure 4. EDX analysis of average elements in zeolite samples [atom %, error ± 2 sigma; total 100%]

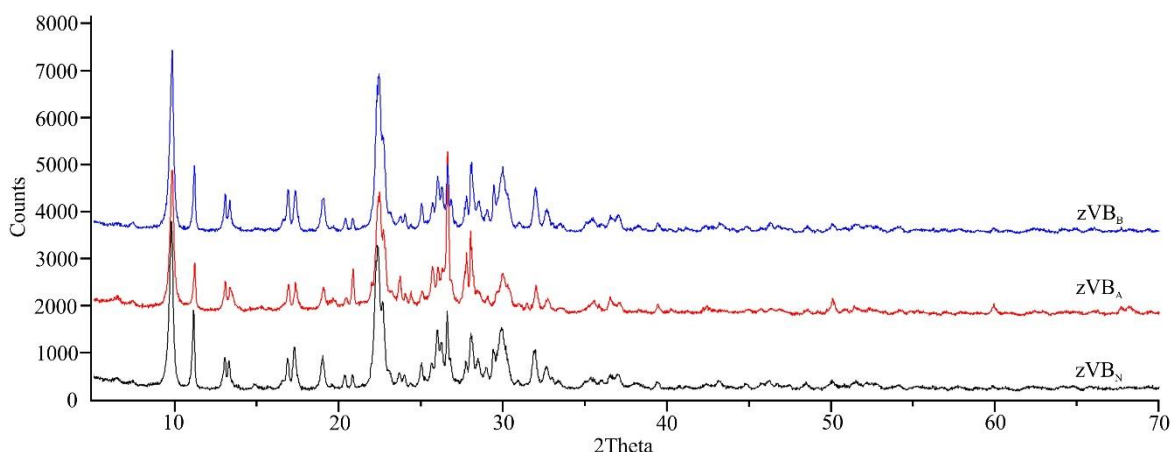


Figure 5. XRD diffractograms of zeolite samples

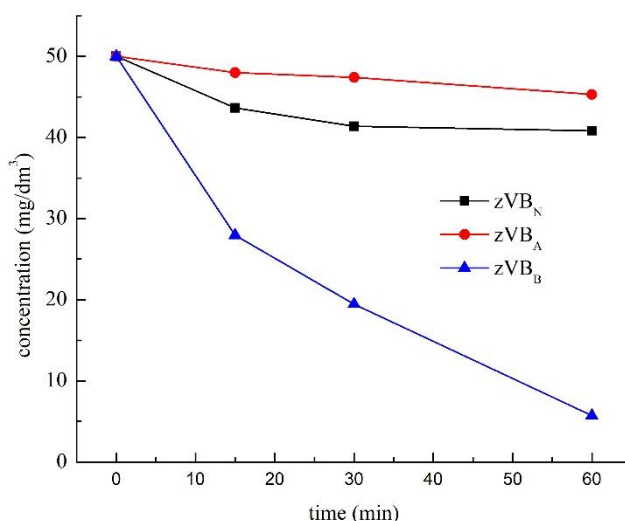


Figure 6. Effect of contact time on the removal of Cu(II) by zeolite materials

Table 1. Textural properties of the zeolite samples

Sample	BET surface area $S_{BET}(m^2g^{-1})$	Average pore diameter (nm)	BJH cumulative desorption pore volume (cm^3g^{-1})
zVB _N	22.87	15.42	0.0863
zVB _A	21.47	15.17	0.0746
zVB _B	31.79	15.39	0.1316

Preliminary sorption results. The preliminary results of the sorption abilities of the obtained zeolite (particle size 0.8-1.25 mm) materials toward copper(II) ions in aqueous solution are shown in Figure 6. These results indicate that raw unmodified natural zeolite (zVB_N) and zeolite modified with hydrochloric acid (zVB_A) show similar, but not significantly efficient sorption properties. Copper removal efficiency, RE (%) is *ca.* 19% for zVB_N and *ca.* 10% for zVB_A. By treatment with sodium hydroxide (zVB_B) better sorption properties (RE, *ca.* 90%) than zVB_N and zVB_A for removal of Cu(II) ions from wastewater were achieved. The concentration of copper declined sharply with contact time in the first 15

minutes and continued this trend in the range of investigated contact time.

Clinoptilolite is a porous crystal material, which adsorption properties are strongly related to the framework structure, which has performance for physical adsorption and ion exchange [17]. According to the ion exchange mechanism, ions present in the pores of zeolite crystalline lattices are substituted by toxic metal ions from the solution. The ion exchange process is reversible, and the zeolite may be recovered for further use [14].

Surface area analysis. Table 1 summarizes the results of the textural properties of the tested zeolite samples. In comparison with the results of other authors, very similar values of specific surface area,

mean pore diameter and pore volume were determined for (unmodified) raw zeolite (zVB_N) and the acid treated zeolite (zVB_A) [18]. A sample of zeolite treated with NaOH (zVB_B) shows a significant increase in the BET specific surface area and BJH cumulative desorption pore volume. Increase in the specific surface area of the sample (zVB_B) can be possibly related with the phenomenon of presence of cations or minerals which block the pore channels, so the limited extent of zeolite crystalline structure reduces its sorption activity [19], but treatment with NaOH produces an improved adsorbent which is confirmed by the results of the adsorption. The increase in the mesopore volume of the NaOH-treated clinoptilolite is probably caused by unblocking of the channels of the aluminosilicate framework structure of the zeolite through dealumination and decationation during base leaching, and possibly also by dissolution of any amorphous silica

blocking the channels of the clinoptilolite structure [20]. All of the above leads to the improvement of the adsorption activity of the mentioned (zVB_B) zeolite sample.

The N_2 adsorption/desorption isotherms of the zeolite samples showed a typical *s*-shape behavior of IV-type with a type-H3 of hysteresis loop that indicated the existence of mesopores (Figure 7a). The clinoptilolite samples have characteristic presence of this type of hysteresis loop, which can be attributed to multilayer adsorption followed by capillary condensation either in mesopores of impurities (feldspars, quartz, etc.) or in the space developed between the zeolite crystallites [21]. The pore system of all tested zeolite samples is in the meso-pore range between bimodal distributed pores characterized with maxima in pore size between 2–5 nm and 10–50 nm with an average pore diameter around 15 nm in size according to the BJH desorption isotherms (Figure 7b).

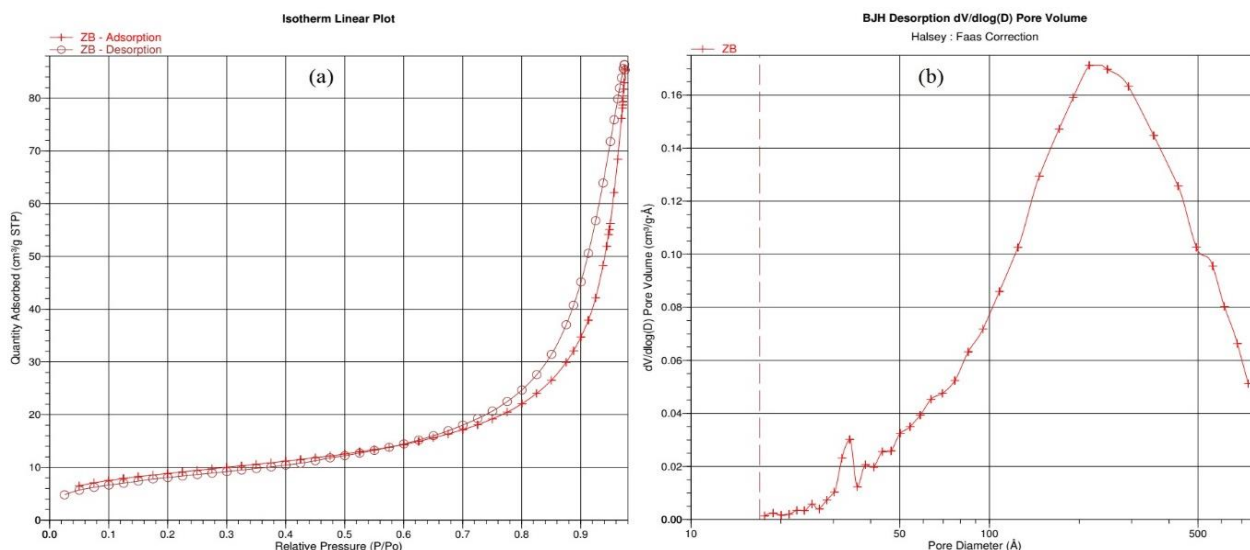


Figure 7. N_2 adsorption/desorption isotherm of zVB_B sample (a) and pore size distribution for zVB_B sample (b)

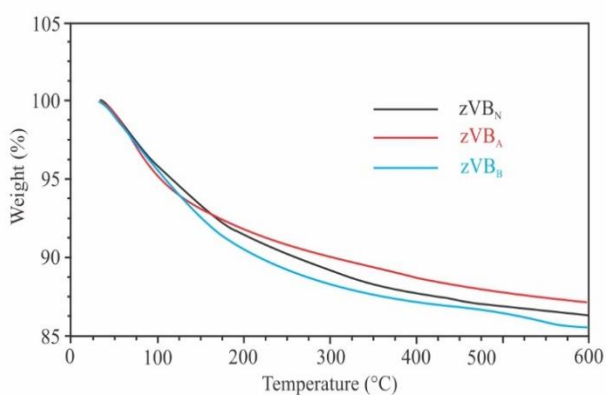


Figure 8. TG curves of the zeolite samples

TG analysis. The results of thermogravimetric analysis of the tested zeolite samples are summarized in Figure 8. Thermal treatment of the

zeolite samples leads to a loss of mass in the range 20–600 °C, because of surface dehydration and dehydroxylation.

The process of zeolitic water elimination is held in a few stages. At temperatures below 100 °C physically adsorbed water is mainly eliminated, further increase of temperature in the range 100–300 °C or higher, leads to removal of hydroxyls through the associative desorption mechanism. At temperatures in the range 200–600 °C almost all hydroxyl groups leave the surface, moreover the isolated OH groups are eliminated at higher temperatures. Changes in temperature of zeolitic water elimination can be a consequence of the presence of different exchangeable cations in zeolites [22]. Based on the results of the

thermogravimetric analysis of the tested zeolite samples presented in Figure 8 it can be noticed that the elimination of intact water is observed up to 120 °C. The most essential loss of mass is observed at 120-400 °C because of associative desorption of hydroxy species and desorption of intact water. A sample of zeolite (zVB_B) treated with NaOH shows the largest loss of mass (ca. 14.50 %), unlike the samples zVB_K and zVB_N with mass loss (ca. 12.90% and ca. 13.70 %, respectively), which can be possibly related to the increase in the specific surface area of the sample (zVB_B). Moreover, differences in TG curves presented in Figure 8 can be related to differences in complex connectivity of pores and variation in their sizes as a result of exchangeable cation replacement with protons.

CONCLUSION

According to the obtained results based on FTIR, XRD, SEM-EDX, TGA and BET analyses, the investigated zeolite from Zlatokop deposit (Serbia) is aluminosilicate material with defined crystal structure and high quality (ca. 90% clinoptilolite) with a pore system in the meso-pore range. Preliminary results of the investigated zeolite materials zVB_N, zVB_A and zVB_B toward removing copper(II) ions from aqueous solution showed good sorption characteristics of zVB_B zeolite (particle size 0.8 – 1.25 mm), which is in accordance with the data obtained by BET and TGA analyses. Since these were preliminary sorption tests, zeolites (raw and activated) will be further examined with the aim to improve their sorption properties, both for inorganic and organic water pollutants, under different experimental conditions (longer contact time, different particle size of zeolite – using natural zeolite with much smaller particle size (zeolite powder), temperature, dose of sorbent, etc.).

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