

REMOVAL OF Cr(VI) FROM WATER RESOURCES BY USING DIFFERENT RAW INORGANIC SORBENTS

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Abstract: Natural minerals from different localities in the Republic of Macedonia are selected for elimination of Cr(VI) ions from water resources. For that aim are selected: aksil (Kriva Palanka), trepel (Bitola), SiO₂ amorphous (Kozuf), pemza (Bojanciste). In this study, their adsorption capacity is analyzed using spectrophotometric method (UV/VIS Spectrophotometer). Results from the spectrophotometric analysis in all used examples gave us insight for the starting concentration of Cr(VI) before adsorption and concentration after adsorption. The physical, chemical and mineralogical characteristics of adsorbents are studied. XRD, TGA-DTA and FT-IR analysis are used for characterization of natural mineral materials. The surface area of the sorbents were measured by BET method. With aim to determine the optimum pH value for maximal removal of Cr(VI) ions, the point of zero charge, pH_{pzc}, for investigated materials were obtained. The aim of the study is to select which adsorbent is more efficient for elimination of Cr(VI) from water resources. According to obtained results all of them were successful in elimination of Cr(VI), but more efficient and economic is trepel.

Keywords: Cr(VI), water resources, adsorption, natural minerals.

Introduction

In the modern society, the management of the water resources is very important for the environment protection. The water pollution with heavy metals is one of the biggest environmental problems because of their toxicity. Therefore, the removal of the heavy metal ions from water and wastewater is very important for environmental protection, and thus the public health. Chromium is ranked as most toxic pollutant of wastewaters. The Cr(VI) ions are toxic, carcinogenic and mutagenic to all life forms and is considered a major pollutant (Norseth 1981; USDHHS 1991; Cieslak-Golonka 1995; Myers et al., 2000; Zhitkovich et al., 2002 and Dupont, Guillon 2003). Cr(VI) is used in many industries such as: manufacturing of paints, metal works, manufacture of automobile parts and in the petrochemical industry (Chakir et al., 2002). Wastewaters from these industries contain large amounts of chromium that is spread to the environment through land, water and eventually accumulate in the food chain. International Agency for Research on Cancer has classified as carcinogenic chromium (Biswajit et al., 2013). Limit of Cr(VI) in the wastewater is only 0.05 mg/l (ATSDR 2002). Therefore concentrations of Cr(VI) must be reduced to such an extent as to meet environmental regulations. Conventional methods for removal of ions of heavy metals from water and wastewater are chemical precipitation, ion exchange, electrochemical deposition, solvent extraction, membrane filtration and adsorption (Patterson 1977; George 1985; Tiravanti et al., 1997, Dahbi et al., 1999 and Naiya et al., 2009). The removal of chromium, Cr(VI), is tried with adsorbents such as activated carbon (Srivastava et al., 1996), Spirogyra Biosorbents (Gupta et al., 2001), floating ashes (Bayat and Gupta 2004) etc. In recent years, the elimination of heavy metals from wastewater is achieved by using certain types of natural or agricultural waste (Chatterjee et al., 2010, Khambhaty et al., 2009), sunflower handle (Sun and Shi 1998), bark of Eucalyptus (Sarin 2006), bran of corn (Singh et al., 2006), shell of coconut, leaves of trees, shells of peanuts and nuts (Karthikeyan et al., 2005). In this work four different adsorbents (aksil,

trepel, SiO₂ amorphous, pemza) were used for the removal of hexavalent chromium, Cr(VI).

Materials and Methods

ADSORBENT

The aksil, used as adsorbent for Cr(VI) removal from aqueous solutions was collected in Kriva Palanka. The trepel was collected in Suvadol, Bitola. SiO₂ amorphous in Kozuf. The pemza is from deposit site called Bojanciste, near Kavadarci. The investigated raw inorganic samples in this study were used in their natural state without any treatment.

Reagents and Chemicals

Standard solution of dichromate potassium, K₂Cr₂O₇ (1 g/dm³), hydrochloric acid, HCl (0.1 M), sodium hydroxide, NaOH (0.1 M). All the reagents and chemicals used in the experiment were analytical grade.

CHARACTERIZATION METHODS

The pH of the solution was measured with the GMH 3500 Series-Greisinger, Germany. Spectrophotometer (UV/VIS Prove 600) was used to determine the Cr(VI) concentration in standard and treated solutions after adsorption experiments. X-ray analysis were recorded on DRON instrument, radiation CuK α . FT-IR analysis were recorded on Perkin Elmer FTIR 2000 instrument with the use of a method of the pressed tablet of KBr. TG/DTA analysis were measured by Perkin Elmer -7 DYAMOND System, in air, with heating rate of 10 K/min, using ~ 15 mg of sample. For determination of the point of zero charge, PZC, of the natural minerals 0.2 g material was weight and then transferred to a 300 ml Erlenmeyer flasks to which 100 ml of distilled water, with varying pH (pH_{initial}) from 2 to 10, were added. The initial pH was adjusted by adding either HCl or NaOH solutions. The Erlenmeyer flasks were continuously shaken in an laboratory shaker with 140 rpm for 24 hours at room temperature. Then the suspensions were filtered and pH (pH_{final}) of each filtrate was measured. The surface area was measured using static gravimetric method.

ADSORPTION EXPERIMENT

Standard solution of K₂Cr₂O₇ with concentration of 1000 mg/l was used to prepare solution with initial Cr(VI) concentrations of 0.5 mg/l. This solution was placed in 11 beakers and 2.5 g of dry natural inorganic adsorbents was added into each beaker. The mixture of adsorbent and Cr(VI) solutions with initial concentrations of 0.5 mg/l, were stirred using magnetic stirrer at 400 rpm, at pH of the solution 3, at room temperature. pH of the solution adjusted by adding HCl solution as required. The samples were taken at particular time, filtered and filtrates were collected for analysis and the remaining Cr(VI) concentration was determined using UV-visible spectrophotometer using 1.5-diphenylcarbazide method as laid down in standard methods for examination of water and wastewater (APHA, AWWA, WEF 1998 edition). Also the remaining concentrations of Cr(VI) ions in the filtrate were determined using atomic absorption spectrophotometer, AAS Perkin Elmer model AA700.

Results and Discussion

MATERIAL CHARACTERIZATION

The BET surface area a_s , [m²/g] was measured using gravimetric method. Obtained the following values: aksil 122.56; trepel 57.64; SiO₂ - amorphous 63.26; pemza 7.92 m²/g.

The chemical composition of the aksil, trepel, pemza, SiO₂ amorphous are given in Table 1.

From a chemical composition, sample aksil represents acidic metallic material where the percentage of SiO₂ is between 58.0 to 62.0%. The percentage of Al₂O₃ ranged from 16.8 to 18.0% while the percentage of Fe₂O₃ is in the range from 4.0 to 5.0%. Alkaline earth oxides CaO 5.0-6.0%, MgO 2.2-2.7% while alkaline oxides K₂O 2.3-2.7%, Na₂O 3.0-3.2%. The chemical composition of the sample aksil is given in Table 1.

Table 1. Chemical composition of the aksil, trepel, pemza, SiO₂ amorphous [wt.%]

Oxides	Aksil wt. %	Trepel wt. %	Pemza wt. %	SiO ₂ amorphous wt. %
SiO ₂	58.0-62.0	64.95	63.73	92.97
Al ₂ O ₃	16.8-18.0	11.85	17.48	1.52
Fe ₂ O ₃	4.0-5.0	4.51	3.10	0.21
CaO	5.0-6.0	1.49	2.50	0.43
MgO	2.2-2.7	1.88	0.59	0.19
K ₂ O	2.3-2.7	1.40	4.95	0.26
Na ₂ O	3.0-3.2	0.84	4.45	0.08
SO ₃		1.74	-	0.05
LOI	4.2-4.5	11.20	3.07	3.86
Total		99.86	99.86	99.73

Chemical composition of trepel show that it is acidic rock with about 60% SiO₂. The chemical composition of trepel is shown in Table 1. The parameters of the quantity present SiO₂ and Al₂O₃, and loss of weight (LOI) obviously point to the established mineral fazes- opal, illite, quartz, feldspar, chlorite in treated sample. The total content of alkaline oxides in 2.53% point to content of 16% feldspat. The contents of Fe₂O₃ (6.57%) and MgO (2.16%) are compatible with the designated (Mg, Fe)- hlorit in sample of trepel. Pretty low CaO content with 2.60% indicating that the determined plagioklas belongs to albite-type oligoklas.

From a chemical composition pemza can be classified in the group of acidic silicate materials as the percentage of SiO₂ is 63.73%. The chemical composition of pemza Bojanciste is given in Table 1.

Chemical composition showed that the raw material SiO₂ amorphous contains around 93% SiO₂ and if you consider that there are around 3% loss of raw material on heating it can be concluded that it contains only three percent, 3% impurities. The chemical composition of the raw material is pointing to the

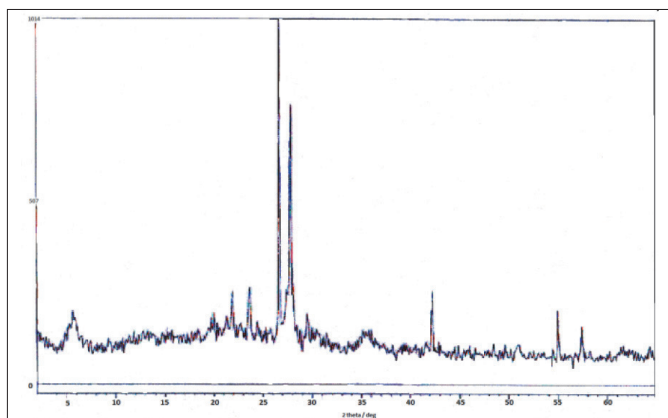


Figure 1. XRD of investigated material (aksil)

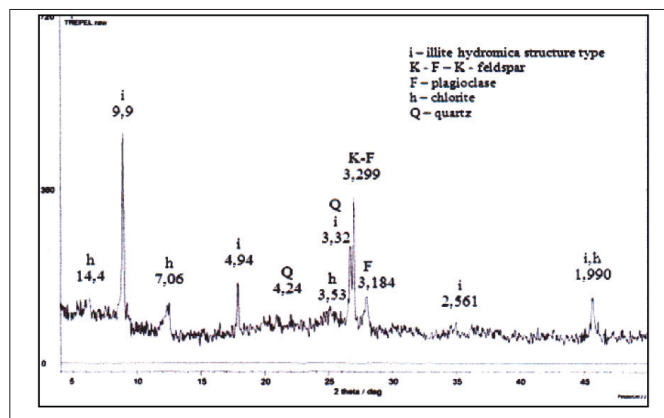


Figure 2. XRD of investigated material (trepel)

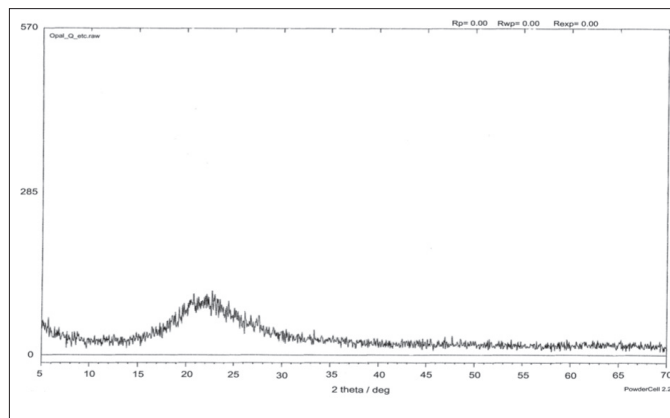


Figure 3. XRD of investigated material

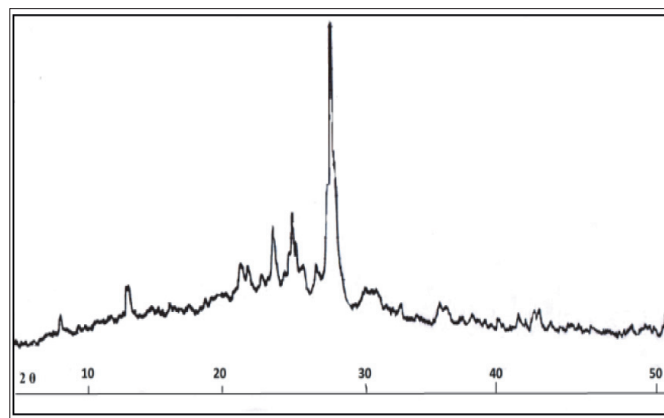


Figure 4. XRD of investigated material (pemza) (SiO_2 -amorphous)

fact that it is a high quality amorphous SiO_2 material. The chemical composition is shown in Table 1.

Mineralogical composition of the samples are studied with X-ray structural analysis by Debye-Scherrer powder method. The results of X-ray examinations of the samples are shown in Figure 1, 2, 3, 4.

The results of X-ray examination of the aksil are presented in Figure 1. From X-ray diffractogram can be concluded that in sample aksil predominates minerals: feldspar, montmorillonite, illite, quartz amorphous phase.

By analyzing trepel with X-rays (DRON, 36 kV, 18mA, $\text{CuK}\alpha / \text{Ni}$) are determined: opal, quartz, illite-hidromika structures feldspati (plagioclase, K-feldspars) and kloriti. The results of X-ray examination of the trepel performed are shown in Figure 2.

The results of X-ray structural studies of natural sample of amorphous SiO_2 are shown in Figure 3. From X-ray structural diffractogram shown in Figure 3 can be concluded that it is amorphous SiO_2 given that the diffractogram only in the range $19\text{-}25^\circ 2\theta$ appear a little broad diffuse peak. This is the area in which lie the most intense peaks of the crystalline modification SiO_2 or quartz, cristobalite and tridimit.

Based on the X-ray diffractogram can conclude the following: pemza Bojanciste bulk of this sample represents roentgen amorphous mass of volcanic glass that has crystallized noble amount of crystalline phase. The crystal phase is composed mainly of minerals from the group of plageoklazi and albite, oligoklas and anorthosite and the amount of potassium feldspati, orthoclase mikroklin. Something smaller quantities than in previous minerals are occurring minerals like quartz, biotite and augi. The results of X-ray examination of the pemza are presented in Figure 4.

Fourier transform infrared spectra (FTIR) for aksil is presented in Figure 5. From figure it can be concluded that adsorption bands at 450 , 792 and 1092 cm^{-1} are as result of presence of quartz in the sample,

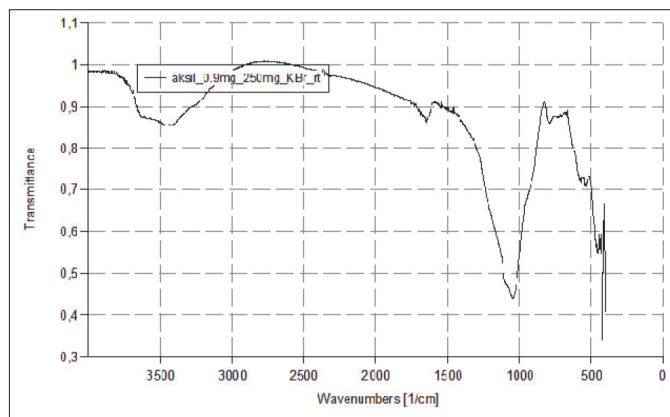


Figure 5. FTIR spectra of the aksil

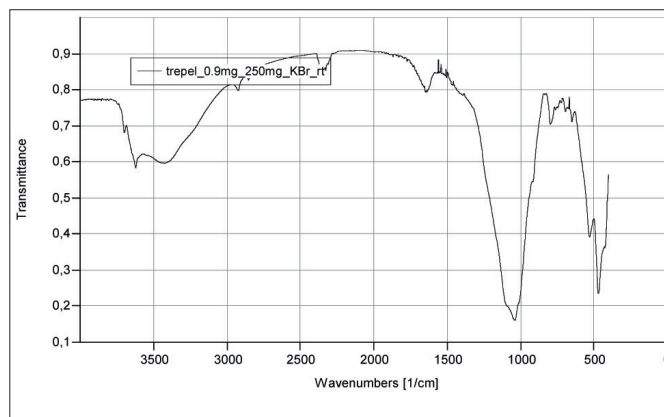


Figure 6. FTIR spectra of the trepel

while the bands at 1042 and 1642 cm^{-1} are due to the presence of amorphous SiO_2 . The strips 535, 575 and 625 cm^{-1} indicate the presence of feldspar in the aksil. Bar at 1642 cm^{-1} and a broad band in the range of 3400 to 3650 cm^{-1} are due to the presence of crystal water and OH^- groups in the clay minerals (illite and montmorillonite) and in the amorphous SiO_2 .

Adsorption bands at 800, 1033 and 1633 cm^{-1} result from amorphous SiO_2 present in the trepel. In this sample the main strip of SiO_2 occurs at 1033 cm^{-1} , moved to smaller values of frequency as a result of the substitution of Si^{+4} ions in tetrahedral position with trivalent cations. The strips 466, 525, 642 and 1083 cm^{-1} indicate the presence of silica in trepel. Strips at 1633, 3450 and 3617 cm^{-1} result from adsorbed water in trepel. The strip at 3690 and deformed band at 936 cm^{-1} indicate the presence of hydroxyl groups in trepel. FTIR spectrum of the trepel is shown in Figure 6.

In Figure 7 is shown the infrared spectrogram of studied natural amorphous SiO_2 .

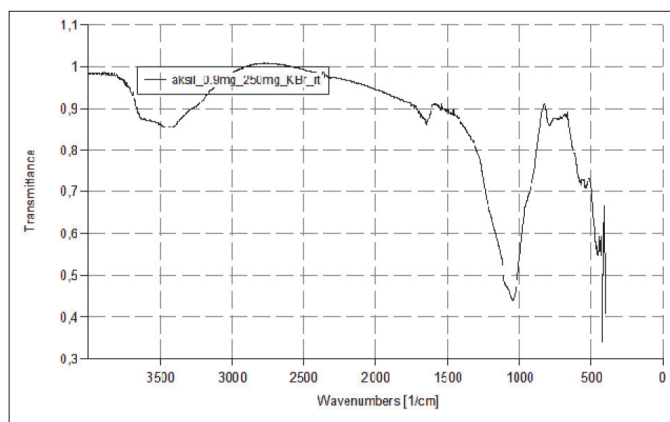


Figure 7. FTIR spectrum of natural amorphous SiO_2

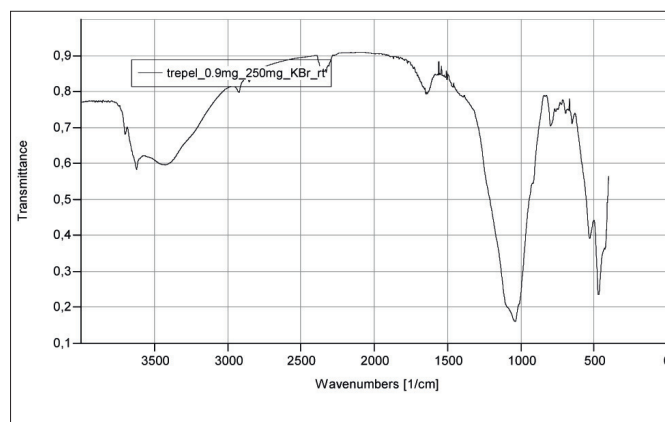


Figure 8. FTIR spectra of pemza

Adsorption bands at 1620, 1067 and 800 cm^{-1} are due to the amorphous SiO_2 present in the diatomaceous earth. The main SiO_2 -band at 1067 cm^{-1} is marginally moved to smaller values of frequency. This shift of silicon oxygen strip is due to the substitution of Si^{+4} ions in tetrahedral position by trivalent ions. In the range of 500 to 800 cm^{-1} is indicated the existence of so-called composite tape that occur due to the presence of three-valent ions and are known as silicon-oxygen- Me^{+3} bands. Wide strip occurs at 3045 cm^{-1} due to the present adsorbed H_2O and hydroxyl groups present in the sample. Strip at 1063 cm^{-1} is due to SiO_2 present in an amorphous state and adsorbed water. Strip that appears at 480 cm^{-1} is due to Si-O-Si bond and the resulting minimum presence of quartz and cristobalite in the sample. Wide deformed strip which appears at 3620 cm^{-1} is due to hydroxyl groups present in the sample.

Fourier transform infrared spectra (FTIR) for pemza is presented in Figure 8. From figure it can be concluded that adsorption bands at 1642, 1033 and 800 cm^{-1} resulting from the present amorphous SiO_2 in pemza. Bands at 442, 583 and 800 cm^{-1} occur as a result of presence of volcanic glass (alkali aluminosilicate glass) in pemza. Bands at 550, 630 and 720 cm^{-1} due to the present feldspati in pemza. Broad band at 3450 and 3617 cm^{-1} resulting from the adsorption of pemza in water. While the strips 3450 and 3700 cm^{-1} show the presence of hydroxyl groups in pemza.

Differential thermal and thermogravimetric analysis (DTA/TGA) for aksil is presented in Figure 9. From thermogravimetric curve it can be concluded that from room temperature up to 700 $^{\circ}\text{C}$ have continuous loss of weight. This weight loss at low temperatures to 120 $^{\circ}\text{C}$ is due to dehydration of the sample. The loss of weight at temperatures above 120 $^{\circ}\text{C}$ is due to removal of crystal water and OH^- groups of clay minerals and amorphous SiO_2 . Exothermic peak shown in the DTA curve at 325 $^{\circ}\text{C}$ is resulting from the present mineral illite in aksil.

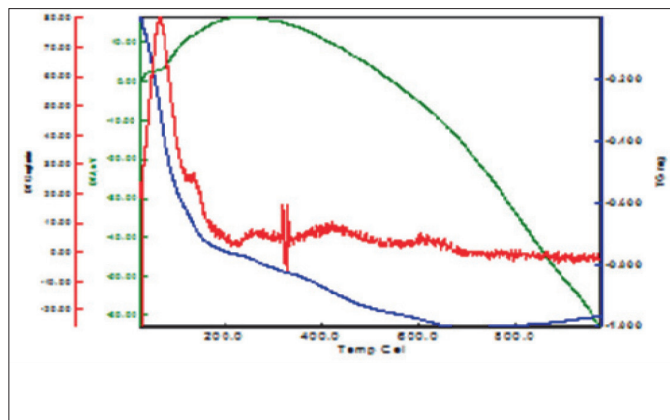


Figure 9. DTA/TGA of the aksil

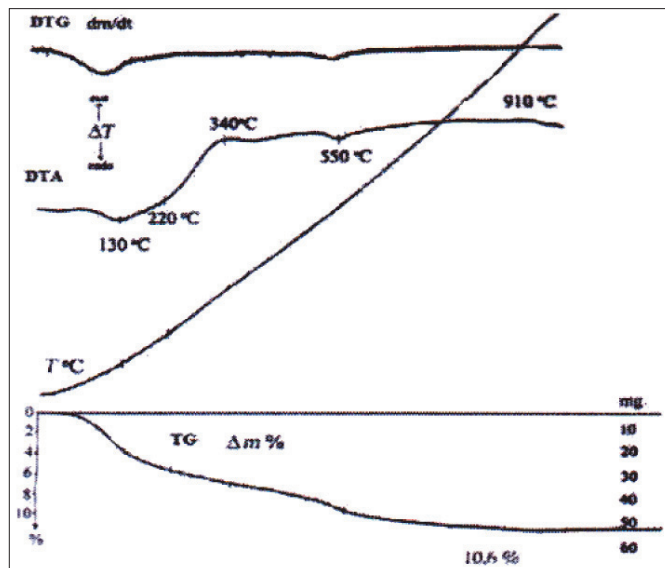


Figure 10. DTA/TGA of the trepel

Differential thermal analysis and termogravimetric analysis of trepel compatible with x-rays tests. In DTA curve can be seen very wide endo-peak that begins about 80°C to 300°C with a minimum of 150°C corresponding to the opal and mineral ilit-hidromika structure. Other thermal effects are minor. TG curve shows a total weight loss of 17%, which is compatible with mineralogic composition- the presence of minerals (opal, illite) in an amount of 50-70% cca. Results of the DTA / TGA are shown in Figure 10.

Differential thermal and thermo-gravimetric analysis of amorphous SiO₂ is performed with computerized equipment (Stanton Redcroft, England) under the following experimental conditions: temperature range 20-1200°C, heating rate 10°C/ min, weight of sample-11.7 mg, gas-air environment 3 l/h, bottle (carrier material)–ceramics.

The results of differential thermal analysis and termogravimetric analysis of amorphous SiO₂ are shown in Figure 11:

Differential thermal and thermogravymethric analysis of pemza Bojanciste is made of a powdery material. From the differential thermal and thermogravymetric curve of the test sample shown in Figure 12 can be inferred: pemza Bojanciste early intensive dehydration of the sample lies at 180° and ending at 350°C. As a result of intensive dehydration, the differential thermal curve occurs slightly set off endothermic peak. In this temperature range, the sample lost 79.3% of the total content of bound water. Within the temperature range of 350-480°C comes to the establishment of apparent equilibrium and then in the interval 480-720°C again comes to dehydration but much weaker compared with the same in the range of 180-350°C. Dehydration process practically finishes at 800°C.

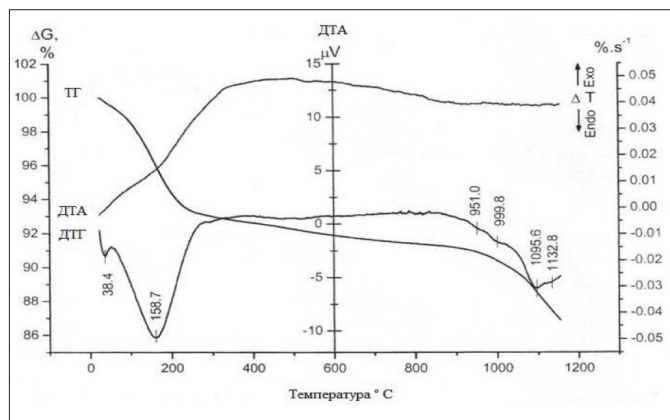


Figure 11. DTA/TGA of the SiO₂ amorphous

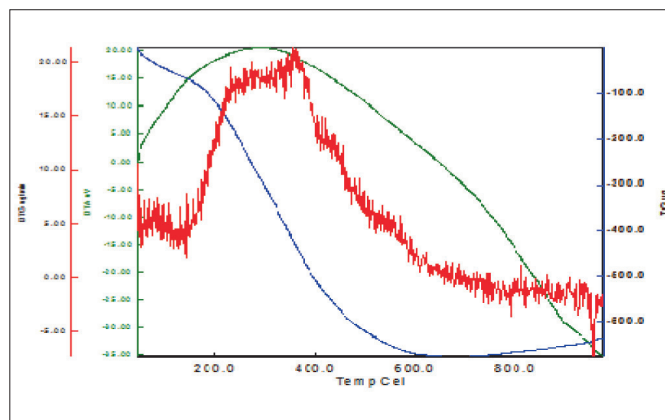


Figure 12. DTA/TGA of pemza

The point of zero charge of an adsorbent surface corresponds to the pH (pH_{pzc}) at which the surface has a net natural charge. The point of zero charge of the samples defined as the pH value of the plateau on the graph of dependence $\text{pH}_{\text{final}} = f(\text{pH}_{\text{initial}})$. The pH_{pzc} represents that pH value above which the removal of cations will be favored. In this case, the optimal pH is in the range of 2 - 4, because chromium ions are in the form of HCrO_4^- .

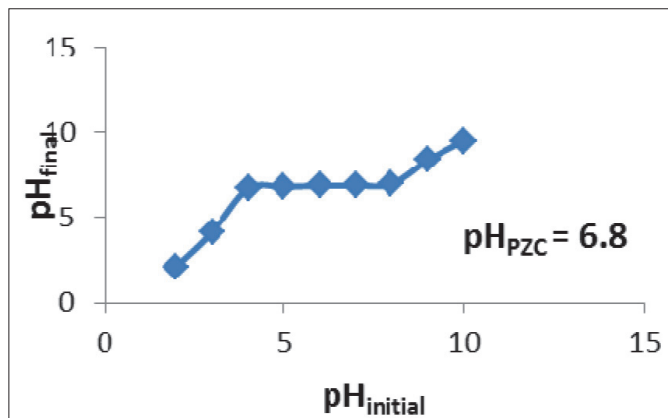


Figure 13. Point of zero charge of the aksil

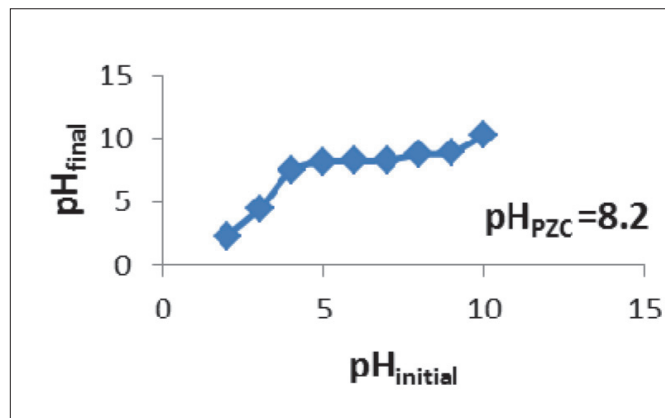


Figure 14. Point of zero charge of the trepel

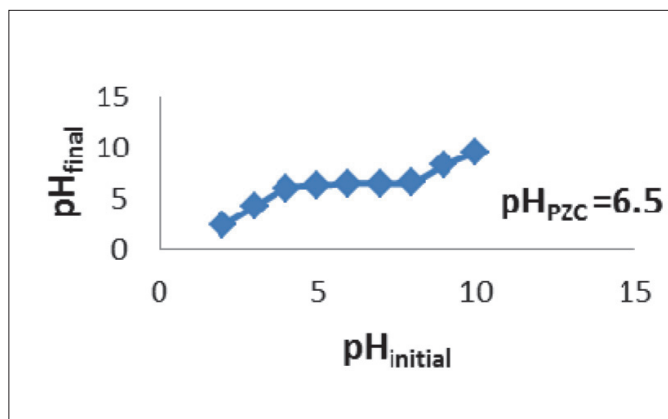


Figure 15. Point of zero charge of SiO_2 amorphous

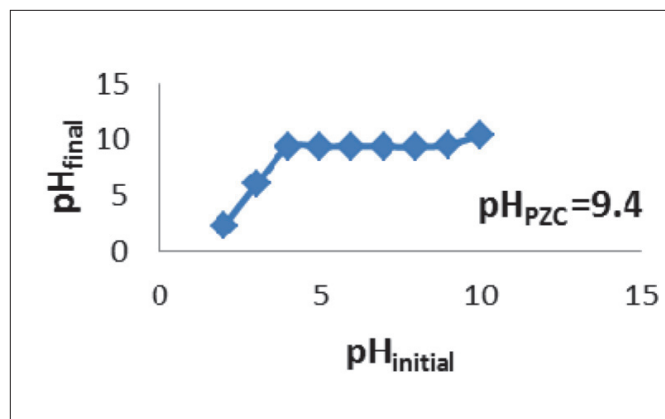


Figure 16. Point of zero charge of pemza

This parameter of the materials is of great importance to define the operating pH range for optimal removal of investigated ion. On the basis of these values, pH_{pzc} can be analyzed and confirmed the phenomenon that happens in the process of adsorption. In general for all tested materials the previous series of experimental results showed that mechanism of elimination is not only on a physical adsorption level of Van der Waals-s forces but there is a complex phenomenon which depending on the structure of the material and surface functional groups incorporates ion exchange and hemisorption.

ADSORPTION STUDIES

All adsorption experiments were conducted at constant room temperature, pH of the solution 3 with an amount of adsorbents 2.5 g/l and initial metal ion concentrations of 0.5 mg/l in batch glass continuously mixed reactor.

The percentage of removal, %R, of Cr(VI) ions was calculated using the following equation:

$$\%R = \frac{C_0 - C_e}{C_0} \cdot 100 \quad (1)$$

where C_0 is initial metal ion concentration [mg/l] and C_e is equilibrium concentration [mg/l].

The dependence of adsorbed amount of Cr(VI) ions from time of adsorption for natural inorganic adsorbents for 0.5 mg/l initial concentrations of metal ions is given in Figure 17. The experiment was conducted using 2.5 g/l adsorbent, at 2l of Cr(VI) solutions with 0.5 mg/l initial concentration, at pH 3, room temperature and 400 rpm. The samples were taken at particular time (5, 10, 20, 30, 60, 90, 120, 150 and 180 minutes), filtered and filtrates were collected for analysis and the remaining Cr(VI) concentration was determined.

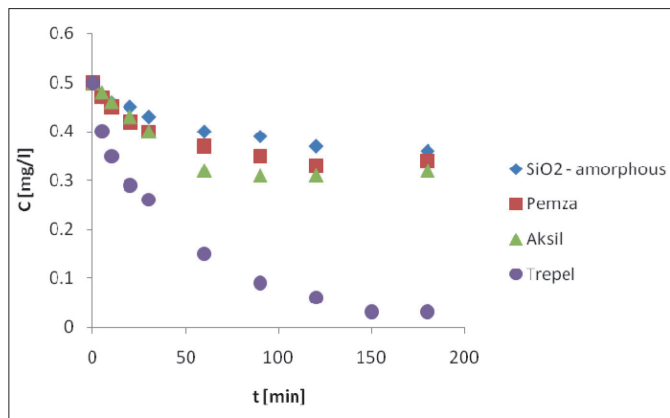


Figure 17. Dependence of Cr(VI) concentration from time of adsorption for the system Cr(VI)-adsorbent

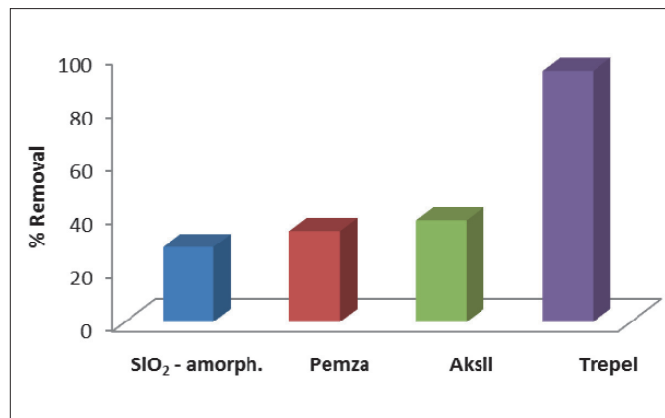


Figure 18. Function of Cr(VI) removal for adsorbents $C_0=0.5$ mg/l; pH=3

The Figure 18 shows the comparison of percentage of removal of Cr(VI) ions for all used natural mineral adsorbents. It can be seen from the figure that the removal percentage for SiO₂ amorphous is 28%, for pemza 34%, for aksil 38% and trepel 94%. The figure 18 also shows that the trepel is more effective in Cr(VI) ions removal than other adsorbents at the same operating conditions.

Conclusion

In this study, the adsorption of Cr(VI) ions on natural inorganic minerals, was investigated. Investigations of the four natural inorganic materials origin from different localities in the Republic of Macedonia showed that the most effective adsorbent for the elimination of Cr (VI) is trepel. The adsorption characteristics have been examined at pH=3 and 0.5 mg/l initial metal ion concentrations, adsorbent dosages 2.5 g/l. Of particular importance for defining the characteristics of the material is the determination of pH_{pzc} on all tested materials. Based on the determined pH_{pzc} the optimum pH value for maximum removal of chromium Cr(VI) from aqueous solutions are defined. The removal percentage of Cr(VI) at 0.5 mg/l initial metal ion concentration for SiO₂ amorphous is 28%, for pemza 34%, aksil 38% and trepel 94%.

It can be concluded that trepel, an raw inorganic material, could be effectively used as low-cost adsorbent for the removal of chromium ions from aqueous solutions. The obtained results from this investigation show that this natural adsorbent, with its characteristics, represents potential porous material for removal of heavy metals pollutants from different aqueous resources. This material origins from our country and is first time tasted for removal of Cr(VI) ions in this article.

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