

## SEPARATION OF Cr(VI) FROM AQUEOUS SOLUTIONS BY NATURAL BENTONITE: EQUILIBRIUM STUDY

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**Abstract:** Removing hexavalent chromium from contaminated wastewater is very important because of toxicity to living organisms. Chromium is carcinogenic and mutagenic in very low concentration values (sub-ppm). The ability of the natural mineral (bentonite) for adsorption of hexavalent chromium, Cr(VI), from aqueous solutions was investigated. The influence of different physical and physicochemical parameters (pH, amount of adsorbent, adsorbate initial concentration) was examined. For characterization of adsorbent, classical chemical analysis thermogravimetric analysis (DTA/TGA), XRD analysis, FTIR-analysis and determination of specific surface area by BET were performed. For quantitative monitoring of the dynamics of studied system for the presence of Cr(VI) ions in model solutions, the AAS and UV/Vis analysis were used. The obtained experimental results were used for modeling of the equilibrium of the process through the application of software package MATLAB/Curve Fitting Toolbox. Following adsorption isotherms: Langmuir, Freundlich, Langmuir-Freundlich and Redlich-Peterson, are applied for analyzing the equilibrium of adsorption system Cr(VI) ions – bentonite.

**Keywords:** Cr(VI), wastewater, adsorption, bentonite, equilibrium study

### Introduction

Cr(VI) is one of the heavy metals which is widely used in many industries. Industry waste of these contains large amounts of chromium that are distributed in the environment through land, water and eventually accumulate in food chain. The hexavalent form is most damaging for the health due to carcinogens and mutagenic properties. The maximum permissible limit of Cr(VI) in effluents is only 0,05 mg/l, but the concentration in the industrial wastewaters is greater. Therefore concentrations of Cr(VI) must be reduced to such an extent as to meet environmental regulations (Tchobanoglous et al., 2003 and Grady et al., 2011). Many materials are studied for adsorption of heavy metal ions such as red mud (Gupta et al., 2001), silicates (Chiron et al., 2003), zeolites (Jakupi et al., 2016a, Jakupi et al., 2016b, Wingenfelder et al., 2005). Removal of hexavalent chromium, Cr(VI), is also tried with adsorbents such as activated carbon (Srivastava et al., 1996), Spirogyra Biosorbents (Gupta et al., 2001), floating ashes (Bayat 2002, Gupta and Ali 2004) and other different raw inorganic sorbents (Memedi et al., 2016). 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 and Khambhaty et al., 2009). Generally, natural or agricultural wastes contain various functional groups such as hydroxyl, aldehyde, aliphatic acid group, alkene, amide, nitro-aromatic, silicate, sulfonate and others. It is the existence of such functional groups in bio-adsorbents that facilitates adsorption of Cr(VI). Also for this purpose in recent years the effectiveness of removal of hexavalent chromium of low cost natural adsorbents such as sunflower handle (Sun and Shi, 1998), bark 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) was investigated.

The term "bentonite" is not an exact mineralogical name or any material with a definite mineralogical composition or definite chemical and physical properties. Originally this term has been used for a

material of an eastern Wyoming and South Dakota, with grayish green, plastic material in the form of clay. The greatest feature of this material is that treated with water blows (swells). Petrography classifies all clays as bentonites that are formed from powder composed of volcanic minerals montmorillonite, bejdelite or mixed together. Since bentonite is composed of materials with different chemical properties and different bentonite have different chemical and physical properties. In the Republic of Macedonia we carried out detailed geological research and concluded that in the Slavishko field there are several mining sites of bentonite clays of sedimentary origin. All known sites differ among themselves on the way to the emergence of the ore and also on the quality. The most significant deposits of bentonite is Ginovci deposit located in north-eastern Macedonia in the area of the village Petralica (Kriva Palanka).

## Materials and Methods

### ADSORBENT

The raw material bentonite, used as adsorbent for Cr(VI) ions removal from aqueous solutions was collected in village Ginovci, Kriva Palanka. The sample in this study was used in the natural form without any treatment.

### REAGENTS AND CHEMICALS

Standard solution of dichromate potassium,  $K_2Cr_2O_7$  (1 g/dm<sup>3</sup>), hydrochloric acid, HCl (0.1 M), sodium hydroxide, NaOH (0.1 M). All the reagents and chemicals used in the experiment were analytical grade (PA).

### CHARACTERIZATION METHODS

The pH of the solution was measured with the GMH 3500 Series-Greisinger, Germany. UV/Vis type Prove 600 was used to determine the Cr(VI) concentration in standard and treated solutions after adsorption experiments by ASTM D6832 standard test method for the determination of hexavalent chromium using 1,5-diphenylcarbazide. X-ray analyses were performed on DRON instrument, radiation  $CuK\alpha$ . FT-IR analyses were performed on Perkin Elmer FTIR 2000. 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,  $pH_{pZC}$ , of the investigated bentonite 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 0.1 M HCl or 0.1M NaOH solutions. The Erlenmeyer flasks were continuously shaken in a 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 gravimetric method.

### ADSORPTION EXPERIMENT

Standard solution of  $K_2Cr_2O_7$  with concentration of 1000 mg/l was used to prepare solution with initial Cr(VI) concentrations of 0.3, 0.4, 0.5 and 0.7 mg/l. This solution was placed in 2l beakers and 2.5 g/l of dry natural inorganic adsorbent was added into each beaker. The mixture of adsorbent and Cr(VI) solutions with initial concentrations, were stirred using magnetic stirrer at 400 rpm, at room temperature. pH of the solution was adjusted by adding  $HNO_3$  solution as required. The samples were taken at particular time, filtered and filtrates were collected for analysis.

## Results and Discussion

### MATERIAL CHARACTERIZATION

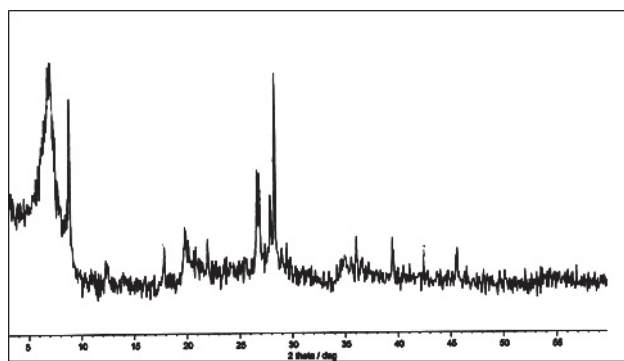
The results of the granulometric sieve analysis show that the fraction of particle size below 0.05 mm corresponds to ~ 90%. The BET surface area ( $a_s$ , m<sup>2</sup>/g) was measured using static gravimetric method. The specific surface of bentonite was 57,64 m<sup>2</sup>/g.

Bentonite from village Ginovci, KrivaPalanka represents polymineral clay with high quality. The chemical composition of bentonite shows that it contains 50-53% SiO<sub>2</sub>, and it can be classified as a neutral silicate raw material. The other most present oxide is Al<sub>2</sub>O<sub>3</sub> in range from 17-19% and the percentage of Fe<sub>2</sub>O<sub>3</sub> ranging from 3-7% (Table 1).

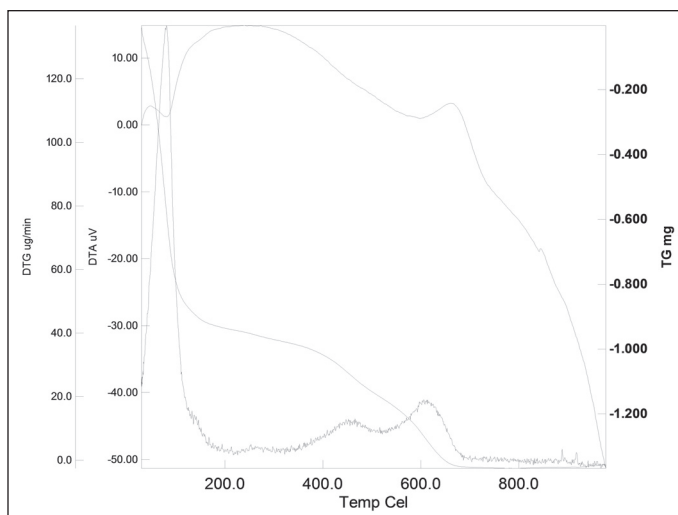
**Table 1.** Chemical composition of the bentonite

| Oxides                         | Bentonite [wt.%] |
|--------------------------------|------------------|
| SiO <sub>2</sub>               | 50.28-52.8       |
| Al <sub>2</sub> O <sub>3</sub> | 17.7-18.5        |
| Fe <sub>2</sub> O <sub>3</sub> | 3-6.5            |
| CaO                            | 1.5-3.4          |
| MgO                            | 1.65-3.3         |
| K <sub>2</sub> O               | 0.3-2.2          |
| Na <sub>2</sub> O              | 0.48-0,80        |

Defining the mineralogical composition of bentonite was performed using the X-ray structural analysis, DTA/TGA and FTIR spectroscopy. The analyze of the obtained results shows that the dominant mineral in the investigated material (natural bentonite) is montmorillonite, which ranges from 75-90%. The other minerals in natural bentonite are: illite which is present in the range of 4-10% while remaining determined minerals such as quartz, feldspars, kaolinite and kristobalite are present in quantities beneath 5%. The results of X-ray examinations of the bentonite is shown in Figure 1.



**Figure 1.** XRD of investigated material (bentonite)



**Figure 2.** DTA/TGA of the bentonite

Differential thermal and thermogravimetric analysis of bentonite was performed under the following conditions: temperature range 20-1100°C, heating rate 10°C/min, sample weight 17.769 mg, gas environment, 10K/min, and carrier material – ceramic. The results of the DTA/TGA of bentonite are shown in Figure 2.

FTIR for bentonite is presented in Figure 3. From figure it can be concluded that adsorption bands at 467, 517, 783 and 1120  $\text{cm}^{-1}$  indicate the presence of silica (Si-O-Si), while the bands at 1034 and 1634  $\text{cm}^{-1}$  indicate the presence of amorphous  $\text{SiO}_2$ . The bands at 617 and 675  $\text{cm}^{-1}$  indicate a link Al-O-Si-O indicate that the presence of feldspati in bentonite. Bar at 917  $\text{cm}^{-1}$  indicates the relationship Al-Al-OH. The bands at 1634, 3442 and 3617  $\text{cm}^{-1}$  indicate the presence of adsorbed water. The bands at 917, 3442 and 3692  $\text{cm}^{-1}$  indicate the presence of hydroxyl groups in the bentonite.

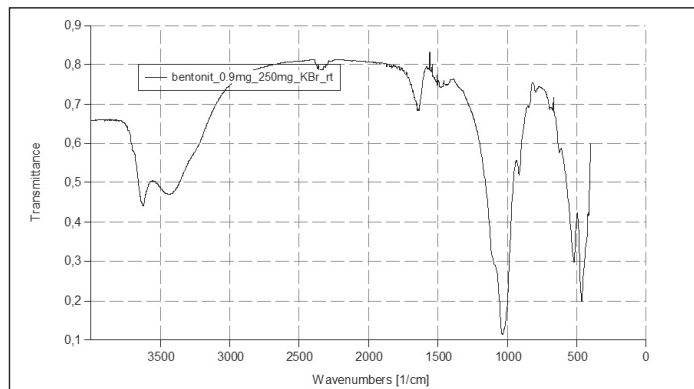


Figure 3. FTIR spectra of the bentonite

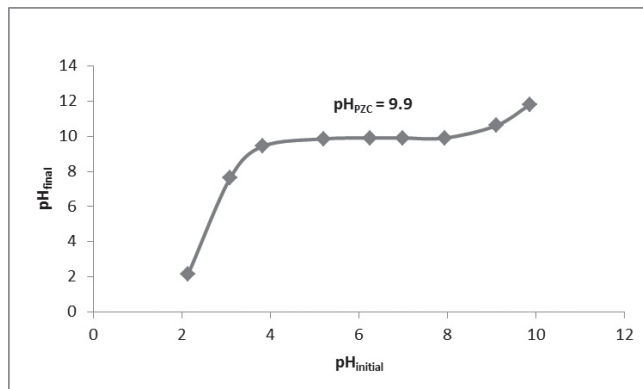


Figure 4. Point of zero charge of the bentonite

The point of zero charge of an adsorbent surface corresponds to the pH ( $\text{pH}_{\text{pzc}}$ ) at which the surface has a net natural charge. This feature of the material is of great importance to define the working pH range in which the removal of adsorbate Cr(VI) will be optimal.  $\text{pH}_{\text{pzc}}$  value of bentonite is shown graphically in Figure 4.

#### ADSORPTION STUDIES

The adsorption experiment was conducted at constant room temperature, pH of the solution 1 with an amount of adsorbents 2.5 g/l and initial metal ion concentrations of 0.5 mg/l.

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

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

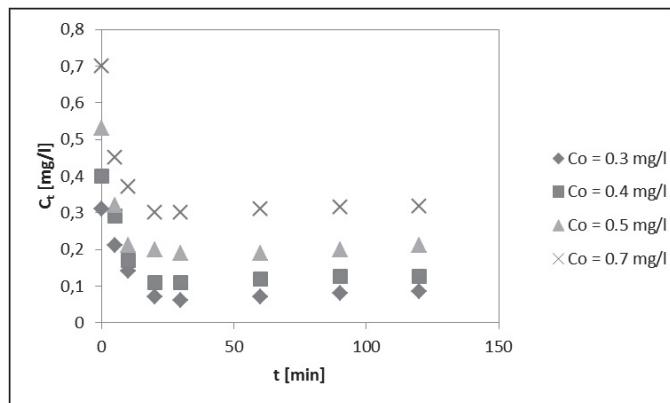
where  $C_0$  is initial metal ion concentration [mg/l] and  $C_e$  is equilibrium concentration [mg/l].

After reaching equilibrium, the concentration of adsorbate,  $q_t$  [mg/g], in the solid phase is determined using the equation number 2:

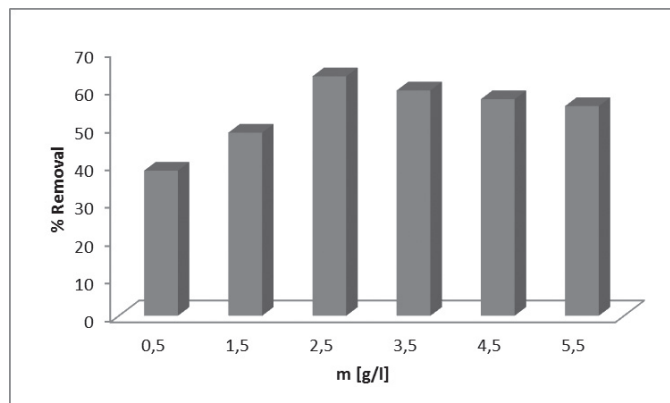
$$q_t = \frac{(C_0 - C_t)V}{m} \quad (2)$$

where  $C_t$  [mg/l] is the concentration of the metal for a time  $t$ ,  $V$  the volume of the solution in a glass [l], and  $m$  adsorbents mass [g].

The dependence of adsorbed amount of Cr(VI) ions from time of adsorption for natural inorganic bentonite for 0.3, 0.4, 0.5 and 0.7 mg/l initial concentrations of metal ions is given in Figure 5. The experiment was conducted using 2.5 g/l adsorbent, at 2l of Cr(VI) solutions, at pH 1, 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. As shown in figures, sorption of Cr(VI) ions on the bentonite increased with an increase of contact time.



**Figure 5.** Dependence of Cr(VI) concentration from time of adsorption for the system Cr(VI)-bentonite



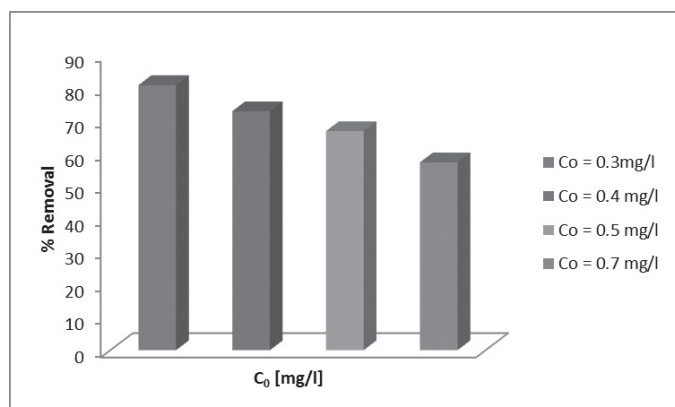
**Figure 6.** Effect of amount of adsorbent to the rate of removal of Cr(VI) ions

### INFLUENCE OF THE AMOUNT OF ADSORBENT

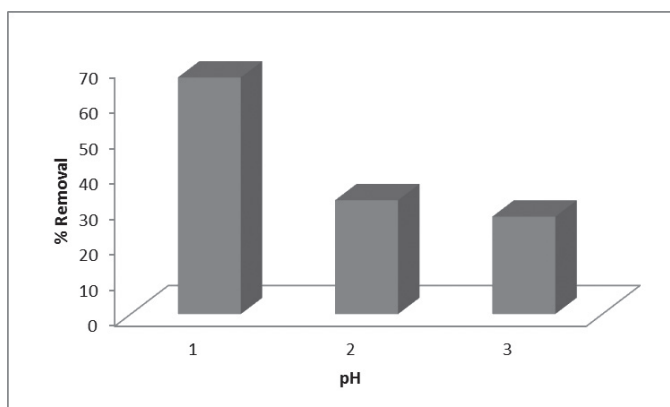
The impact of the quantity of bentonite (0.5, 1.5, 2.5, 3.5, 4.5 and 5.5 g/l) in the degree of removal of Cr(VI) ions, is studied at of the initial metal concentration of 0.5 mg/l, at room temperature, pH 1, 400 rpm and is given in Figure 6. It can be seen that by increasing the amount of adsorbent, the percentage of removal of Cr (VI) increases. Increasing the amount of adsorbent provides greater contact area and availability of more active sites, leading to improve adsorption of examined ions (Kumar and Guar, 2011). In adsorbent amount of more than 2,5 g/l, the removal of Cr (VI) is reduced because of agglomeration of the particles of adsorbent and thus reflected to decrease of the active surface area.

### THE INFLUENCE OF THE INITIAL CONCENTRATION OF THE ADSORBATE IN THE SOLUTION

The impact of the initial concentration in the percentage of removal of bentonite is shown in Figure 7. From the figure it can be seen that the rate of removal increases by reducing the initial concentration of Cr(VI) ions. In the lowest value of the initial concentration the greatest degree of removal of Cr(VI) ions was obtained, 80.65%. The percentage of removal is reduced to 72.71, 66.67, 57.14% with the increase in the initial concentration of Cr(VI) ions of 0.4, 0.5 and 0.7 mg/l, respectively.



**Figure 7.** Effect of the initial concentration to the process of adsorption of Cr(VI) ions in bentonite



**Figure 8.** Function of Cr(VI) removal from pH of the solution

### EFFECT OF pH

The percentage of removal of the Cr(VI) ions is a function of the initial pH value of the working solution. The effect of pH on the Cr(VI) adsorption by bentonite was studied at pH 1,2 and 3, conducting the

experiment at room temperature, with value of initial metal concentration of 0.5 mg/l, constant bentonite amount of 2.5 g/l, volume of the solution 2l, at 400 rpm. The effect of the pH on the percentage of removal is given in Figure 8.

The obtained results show that at initial pH = 1 the maximum percentage of removal are determined as a result of modification (activation of surface by protonization) of the adsorbent, natural bentonite. In general adsorption of anion is favored at  $\text{pH} < \text{pH}_{\text{pzc}}$ . At the very low values of pH, ions of chromium exist in the form of  $\text{HCrO}_4^-$ .

### ADSORPTION ISOTHERMS

The experimental values for the equilibrium of the system Cr(VI) ions - bentonite is shown in Figure 9.

The modeling of experimental data on the system Cr(VI) ions - bentonite was performed with four equilibrium isotherms: Langmuir, Freundlich, Langmuir-Freundlich and Redlich-Petersons, using MATLAB/ Curve Fitting Toolbox software. Selecting the proper isotherm is important for determining the maximum adsorption capacity of the material and equilibrium model parameters. This methodology is important for the kinetic study and design of the system in continuous conditions.

The modeling of the experimental data for the investigated system applying these four models are given in Figure 9.

The value of equilibrium model parameters of the applied adsorption isotherms for studied system presented in Table 2.

| Isotherm            | Parameters and correlation coefficients | Bentonite |
|---------------------|---|-----------|
| Langmuir            | $q_m$ [mg/g]                            | 0.1833    |
|                     | $K_L$ [l/mg]                            | 17.75     |
|                     | $R^2$                                   | 0.9922    |
| Feundlich           | $K_F$ [l/g]                             | 0.2264    |
|                     | $n$                                     | 3.363     |
|                     | $R^2$                                   | 0.9991    |
| Langmuir-Freundlich | $q_m$ [mg/g]                            | 14.19     |
|                     | $K_C$ [l/mg]                            | 0.0241    |
|                     | $n$                                     | 1.85      |
| Redlich-Peterson    | $R^2$                                   | 0.9277    |
|                     | $K_{RP}$ [l/g]                          | 819.6     |
|                     | $A$ [l/mg]                              | 2888      |
|                     | $\beta$                                 | 0.5831    |
|                     | $R^2$                                   | 0.9780    |

Table 2. Model parameters of the applied adsorption isotherms

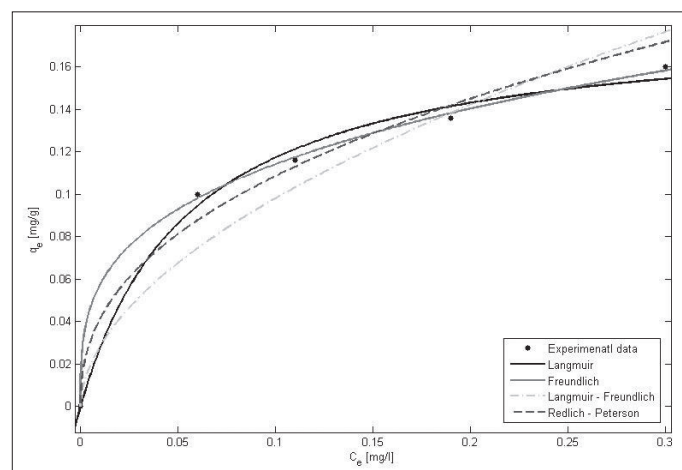


Figure 9. Modeling of the experimental data for the system Cr(VI)-bentonite

Based on the coefficients of correlation it can be concluded that the equilibrium experimental results best fit to the Langmuir and Freundlich adsorption isotherms.

### Conclusion

For the realization of the objective in this paper as starting raw material is used bentonite from Ginovci village, Kriva Palanka. The effect of operating parameters: initial concentration of adsorbate (0.3,



0.4, 0.5 and 0.7 mg/l), time of the adsorption (5 - 180 minutes), pH value 1, 2 and 3 and adsorbent concentration (0.5 – 5.5 g/l) to the process of removal of Cr(VI) ions and the adsorption capacity of the used adsorbent is studied.

The optimal experimental obtained results of the investigated parameters that give the maximal removal of the Cr(VI) ions are: initial metal ion concentration of 0.3 mg/l, pH = 1, and 2,5 g/l of bentonite.

The equilibrium experimental results were best fitted with Langmuir and Freundlich adsorption isotherm models with coefficients of correlation higher than 0.99.

It can be concluded that used natural raw bentonite from micro locality in Macedonia represents effective adsorbent for removal of Cr(VI) ions from aqueous solutions.

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Received: 14.5.2017.

Accepted: 10.6.2017.