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Efficiency of removal Cr(III), Ni(II), Pb(II) ions from simulated wastewater using natural and modified Ca - bentonite

Abdel Đozić[1], Hana Alihodžić[2], Halid Junuzović[3], Indira Šestan[4], Mirnesa Zohorović[5] Melisa Ahmetović[6]

[1]Department of Environmental Engineering, Faculty of technology, University of Tuzla, Bosnia and Herzegovina
Email: abdel.dozic@untz.ba
[2]Department of Environmental Engineering, Faculty of technology, University of Tuzla, Bosnia and Herzegovina
Email: alihodzichana0@gmail.com
[3]Department of Analytical chemistry, Faculty of technology, University of Tuzla, Bosnia and Herzegovina
Email: halid.junuzovic@untz.ba
[4]Department of Physical chemistry and Electrochemistry, Faculty of technology, University of Tuzla, Bosnia and Herzegovina
Email: indira.sestan@untz.ba
[5]Department of Environmental Engineering, Faculty of technology, University of Tuzla, Bosnia and Herzegovina
Email: mirnesa.zohorovic@untz.ba
[6]Department of Physical chemistry and Electrochemistry, Faculty of technology, University of Tuzla, Bosnia and Herzegovina
Email: melisa.ahmetovic@untz.ba

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Abstract— *The aim of this study was to investigate removal efficiency of heavy metals and the adsorption capacity of natural Ca-bentonite, as well as thermally and acid-activated Ca-bentonite (with HCl and H_2SO_4) for the removal of heavy metal ions Cr(III), Ni(II) and Pb(II). The adsorbent used is bentonite from the Shipovo (Šipovo mine), Bosnia and Herzegovina. The results show that the efficiency of heavy metal ion removal using Ca-bentonite is at a satisfactory level. Thus, the highest percentage of removal for the tested metals was at the highest concentration of 20 mg/L, while the decrease in concentration decreased the efficiency of removal of heavy metal ions. The highest percentage of removal was recorded for Cr(III) ions, while the lowest was for Ni(II).*

Keywords— ***adsorption capacity, Ca-bentonite, heavy metals, removal efficiency, wastewater***

I. INTRODUCTION

Examining the presence and methods of removal of heavy metals in both wastewater and drinking water has interested many scientists, resulting in many scientific papers. Heavy metals enter wastewater naturally and by human influence. The natural influence include soil erosion, volcanic activities, urban run offs and aerosols particulate, while the human influence include metal finishing and electroplating processes, mining extraction operations, textile industries and nuclear power [1]. Industrial wastewaters contains certain toxic and harmful pollutants, such as organic pollutants, inorganic pollutants and biological pollutants. The most important inorgnic pollutants include elements such as Cr, Cd, Cu, Ni, Pb, As, and Zn [2]. Heavy metals are highly soluble in the water and therefore they can be absorbed easily by living organisms [3]. The exposure of humans to heavy metals can occur through a variety of routes, which include inhalation as dust or fume, vapourisation and ingestion through food and drink [4]. The most common treatments for removing heavy metals from wastewater include chemical precipitation, membrane filtration, ion exchange, adsorption, and co-precipitation/adsorption [5]. The adsorption process is widely used for the removal of heavy metals from wastewater because of its low cost, availability and eco-friendly nature [6]. This process involves a mass transfer by which a substance is transferred from the liquid phase to the surface of a solid and becomes bound by physical and/or chemical interactions [7]. New types of electronic bonds are created by this interaction [8]. Adsorption has been proved to be the best process of water treatment because of its significant advantages [9]. The use of different adsorbents has become a subject of great interest, and there have been continuous efforts to develop new, low-cost, and efficient adsorbent materials [10]. Adsorbent materials include the use of activated alumina, silica gel, carbons, zeolites, polymers, clay and bentonite.

Bentonite is an absorbent aluminium phyllosilicate, which is essentially impure clay consisting mostly of montmorillonite [11]. The bentonite is a widely available and abundant natural mineral, and can be a low cost adsorbent for water and wastewater treatment [12]. This adsorbent is considered as the best candidate for sorption of different kinds of emerging pollutants due to the excellent sorption, physical and chemical properties of bentonite and the ability of modifying bentonite. This can result in an increase in the sorption capacity for different types of pollutants such as heavy metals [13].

Moosa at al., (2015) reported that using bentonite, the maximum Cr(III) removal efficiency was 99.83% for crude bentonite at a concentration of 100 mg/L; 99.84% for thermally activated at a concentration of 75 mg/L; 99.80% for acid-activated bentonite at a concentration of 50 mg/L and 99.83% for thermally and acid-activated bentonite at a concentration of 25 mg/L [14].

Talaat at al., (2011) reported that the highest adsorption capacity for Cd (II), Cu (II), Zn (II), Ni (II), Pb (II) was achieved using Ca-bentonite, and Na-bentonite was most favorable for Cr (III) adsorption [15].

Melichová & Hromada (2013) studied the adsorption properties of natural bentonite from Lieskovac (Slovakia) for the removal of Pb(II) and Cu(II) ions from aqueous solution in a serial adsorption system. The amount of metal ion adsorption was found to increase with initial pH solution, metal ion concentration and contact time, but decreased with the amount of adsorbent. The maximum adsorption capacity of the adsorbent for Pb(II) and Cu(II) ions was obtained from the Langmuir isotherm and was 11.34 mg/g. [16a].

II. METHODS

Determination of the basic composition of Ca-bentonite by X-ray fluorescence

An S8 TIGER 4K spectrometer (X-ray fluorescence wavelength - WDXRF) with X-ray tubes, Rh anode, two collimators (0.23° and 0.46°) and five crystals for analysis was used to determine the elemental composition. The SPECTRAplus software package was used to interpret the WDXRF spectrum. The dried sample is ground in a mill, sieved through a 2 mm sieve, the sample fraction <2 mm is used for analysis.

Determination of heavy metal content in Ca-bentonite

To determine the content of heavy metal ions in Ca-bentonite, the standard method was used as follows. 1 g of Ca-bentonite was digested in a mixture of HNO_3 and HCl, 3:1. After 24 hours, the sample was filtered. The filtrate obtained was then analyzed on an atomic absorption spectrophotometer.

Determination of pH of Ca-bentonite

After a suspension of 4 g of Ca-bentonite and 20 mL of distilled water was homogenized for 1 hour, the pH of the solution was measured.

Determining the point of zero charge

A 50 mL batch of 0.1 mol/L $NaNO_3$ electrolyte solution was made in the pH range of 2 to 10, and the pH of the solution was measured and labeled as pHi. Then 0.2 g of Ca-bentonite was added to a series of $NaNO_3$ electrolyte solution and the suspension was left for 24 hours with occasional homogenization. After 24 hours, the pH of the solution was measured again and labeled as pH_f. Based on the measured values, a diagram $pH_f = f\ (pH_i)$ is created. The pH value that has not changed during 24 hours represents the pH point of zero charge.

Thermal activation of Ca-bentonite

Activation of bentonite by thermal means was performed by annealing at a temperature of 300 °C for 3 hours. The result of annealing is thermally activated Ca-bentonite which is used to remove heavy metal ions from simulated aqueous solutions.

Acid activation of Ca-bentonite

Two strong acids were used for the acid activation of Ca-bentonite, namely HCl and H_2SO_4 with a quantitative concentration of 0.4 mol/L. Ca-bentonite was added to the acid solutions and stirring was continued for 8 hours at 200 rpm. After filtration, the filter paper was dried in an oven at 105 ^oC for 4 hours and sieved through a 75 μm sieve.

Preparation of synthetic solutions of heavy metal ions

Synthetic aqueous solutions of heavy metal ions that simulate wastewater are prepared from certified reference materials at different concentration intervals for these metals. ***Table 1***. shows the initial concentrations (mg/L) of three heavy metal ions simulating wastewater.

Table 1. Initial concentrations of heavy metals

Metals	(mg/L)	(mg/L)	(mg/L)	(mg/L)
Cr(III)	5	10	15	20
Pb(II)	5	10	15	20
Ni(III)	5	10	15	20

Heavy metal ion adsorption process

In 100 mL of a solution of heavy metal ions of different concentrations prepared as described above, 1 g of Ca-bentonite was added and continuous homogenization was performed for 6 hours at room temperature at a speed of 125 rpm. After the filtration process, the residual concentration of heavy metal ions after the adsorption process was determined in the filtrate. The process of adsorption of heavy metal ions (Cr(III), Pb(II) and Ni(II)) from synthetic aqueous solutions (which simulate wastewater) in this paper was performed using the following adsorbents: natural (crude) Ca-bentonite on which no modification was performed, thermally activated Ca-bentonite, acid-activated bentonite with 0,4 mol/L solution of HCl, acid-activated bentonite with 0.4 mol/L H_2SO_4 solution and the adorption procedure was performed for each individual adsorbent as described.

Determination of heavy metal content by atomic absorption spectrophotometry

The 240 Series Agilent Technology atomic absorption spectrophotometer was used to determine the residual concentration of heavy metal ions after the adsorption process.

III. RESULTS AND DISCUSSION

Results of determination of the basic composition of Ca-bentonite by X-ray fluorescence

Table 2. shows the results of determining the basic composition of Ca-bentonite by X-ray fluorescence shown over the corresponding metals.

Table 2. Chemical composition of Ca-bentonite expressed through oxides of the corresponding metals

Oxide content	mass, %
SiO_2	48,28
Al_2O_3	23,04
TiO_2	0,84
Fe_2O_3	4,52
K_2O	0,29
Na_2O	0,22
P_2O_5	0,014
MnO	0,018
CaO	5,92
MgO	1,98
SO_3	<0,02

The highest oxides contents in Ca-bentonite were SiO_2 and Al_2O_3. The results of the chemical composition were almost the same as the results published in previous studies [17], [18], [16b], [19]. The obtained values for SiO_2, A_2O_3, Fe_2O_3 (48.28%, 23.04%, 4.52%) show a similar trend in the results obtained by researchers Abdullahi and Audu who tested two samples of bentonite in parallel and were: (48,16% and 49.87% for SiO_2, 14.86 and 14.98% for Al_2O_3 and Fe_2O_3, respectively: 4.80% and 5.12%). Also the results obtained for SiO_2 are similar to the values reported by Newke et al., (45 weight%); Tabak et al., (48.35% by weight). However, in terms of Fe_2O_3 content, the results obtained are lower than those reported by Newke et al., (11.10 weight%) Tabak et al., (8.26 wt%), but are higher than those published by Kiviranta and Kumpulainen, (3.82% by weight). Laterite or "red earth" consists mainly of iron oxide. Accordingly, the values obtained for Fe_2O_3 in the paper indicate that a low concentration of laterite is present in Ca-bentonite clay. The Na_2O content of the Ca-bentonite sample has much lower values (0.22 weight%) than those reported in the literature by researchers Abdullahi and Audu (1.66 and 1.43 weight%); Newke et al., (2.7% by weight); Tabak et al., (3.65% by weight). The values of MgO and TiO_2 content are similar to those given by Abdullahi and Audu, (2.08 and 0.94% by weight, respectively); Newke et al., (2.5 and 1.68 weight%) while the MgO content values reported by Tabak et al. Are significantly higher (5.47 weight%). In their work, Kiviranta and Kumpulainen obtained higher values for SO_3 (0.7 weight%) compared to the values obtained in this paper (<0.02 weight%). By comparing the results obtained for MnO, in their work, Newke et al. Obtained slightly higher results, namely 0.15

weight%. Based on the above, it can be seen that it is a material that is a significant carrier of aluminosilicates. Since the highest values were recorded for SiO_2 and Al_2O_3, Ca-bentonite belongs to the group of refractory materials.

Results of determination of heavy metal content in Ca-bentonite

The content of heavy metals in the bentonite clay sample is shown in ***Table 3.***

Table 3. Content of heavy metals in Ca-bentonite

Elements in Ca-bentonite clay	Metal concentration (mg/kg)	Limit values for clay soil (mg/kg)
Zn	2,61	200
Pb	31,41	100
Cd	0,56	1,5
Ni	4,08	50
Co	9,86	60
Fe	2224,83	50000
Mn	30,56	1000
Cu	10,79	80
Cr	0,77	100

Limit values of the content of tested metals in the soil are prescribed by the Rulebook on Determination of Harmful and Hazardous Substances in Soil and Methods of Their Testing "Official Gazette of the Federation of BiH", No. 72/09. The Ordinance sets limits for the content of heavy metals for different soil textures (sandy, powdery and clayey) and is expressed in mg/kg. Since Ca-bentonite belongs to the family of clay minerals, only the limit values for clay soil are presented in the paper (***Table 3***.). Comparing the content of tested heavy metals with the limit values, it is clear that the concentrations of heavy metals in Ca-bentonite do not exceed the prescribed limit values. Accordingly, this natural material is very suitable for use in the adsorption process.

Results of determination of pH value of Ca-bentonite

The measured pH value was 8.86. Based on the literature data, it can be concluded that at high pH values the mobility as well as the solubility of heavy metal ions is very low. In general, the solubility as well as the mobility of heavy metals in the soil increases with the acidification of the soil. The pH value of the clay suspension has a strong influence on its technical applications and some important properties, including adsorption and rheological properties [20].

Results of determining the zero charge point

The zero charge point determined for Ca-bentonite is shown in the ***Figure 1***. The value of the zero charge point represents the pH value above which cation removal will be favored. A value of 8.27 can be seen in the figure, ie above this value, the removal of positively charged ions will be more efficient. By comparing the obtained results, it obtained a slightly lower value in its work 7.8 for natural clay [21].

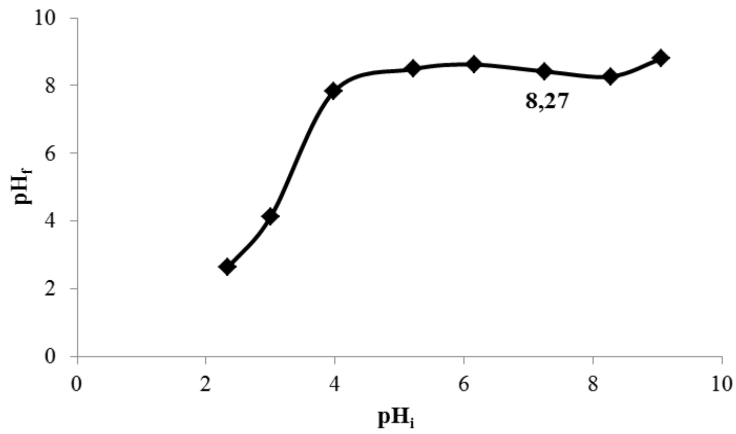

Fig.1. Zero charge point

Results of determining the optimal adsorption capacity

Removal efficiencies of heavy metals Cr(III), Pb(II) and Ni(II) treated with natural Ca-bentonite

Heavy metal ions removal efficiencies Cr(III), Pb(II) and Ni(II) whose initial concentrations ranged from 5 to 20 mg/L with natural Ca-bentonite are expressed as a percentage (%) and are shown in ***Figure 2***. The highest removal efficiency of heavy metal ions was in the order Cr(III)> Pb(II)>Ni(II) (98.56%, 96.03% and 81.50%) at an initial concentration of 5 mg/L. At a concentration of 20 mg/L, the removal efficiency was the lowest, in the order

Cr(III)> Pb(II)> Ni(II) (97.75%, 56.57%, 43.67%). Based on the ***Figure 2.***, it can be conclude that with increasing concentration of heavy metal ions, the removal efficiency decreased. Comparing the obtained results with the results of the author [22a] concluded that an identical trend in behavior occurs, with an increase in the concentration of Cr(III), Pb(II) and Ni(II) there is a decrease in the ion removal efficiency of these heavy metals.

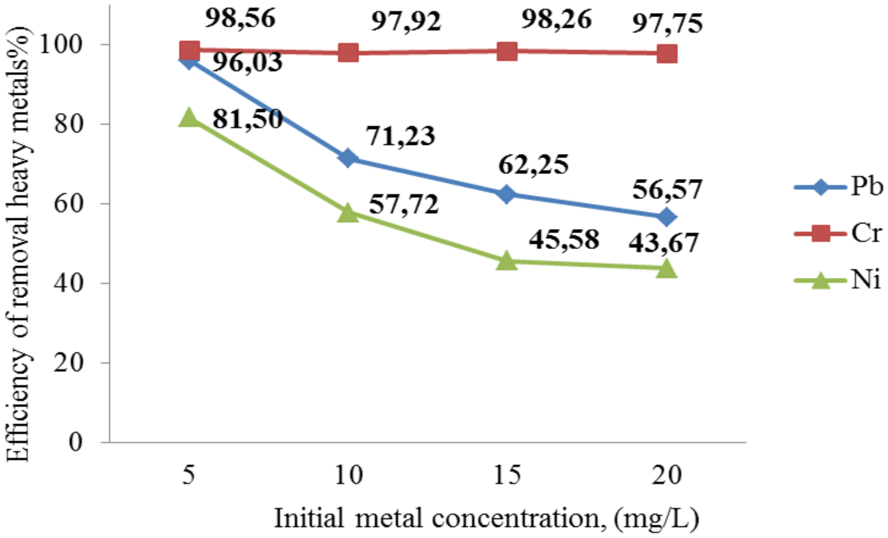

Fig.2. Efficiency of removal of heavy metal ions Cr(III), Pb(II) and Ni(II) treated with natural Ca-bentonite

Heavy metal ion removal efficiencies Cr(III), Pb(II) and Ni(II) treated with thermally activated Ca-bentonite

Similar results were obtained using thermally activated Ca-bentonite where the highest ion removal efficiency was in the order Cr(III)>Pb(II)>Ni(II) (98.08%, 94.15%, 84.24%) at an initial concentration of 5 mg/L. Similar results were obtained at an initial concentration of 20 mg/L, Cr (III)>Pb(II)>Ni (95.80%, 51.03% and 40.23%).

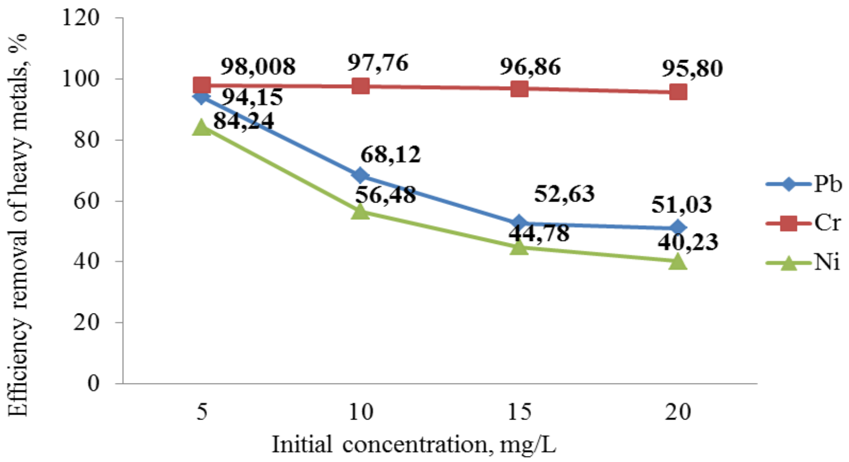

Fig.3. Efficiency of removal of heavy metal ions Cr(III), Pb(II) and Ni(II) treated with thermally activated Ca-bentonite

Removal efficiencies of heavy metals ions Cr(III), Pb (II) and Ni(II) treated with Ca- bentonite activated with H_2SO_4

The highest efficiency of heavy metal ion removal of 97.57%, 81.99%, and 60.37% was in the order Cr (III)> Pb(II)>Ni(II) at the lowest concentrations of these heavy metals, while at higher lower concentrations of heavy metal ion removal were observed in the concentrations and amounted to 86.02%, 60.95% and 36.04% for Cr(III), Pb(II) and Ni(II). [22b] investigated the influence of initial concentrations on the performance of the adsorption process of natural and modified clay activated thermally and with acid (H_2SO_4). What was found is that with increasing concentrations, the adsorption capacity of clay samples (natural, acidic and thermally activated bentonite) for lead and chromium ions also increased. The increase in adsorption with increasing concentration of metal ions is the result of the driving force that the initial concentration allows to overcome the resistance of mass transfer between the aqueous and solid phases. The increase in adsorption capacity indicates that adsorbents have a high potential to remove Pb(II) and Cr (III) ions.

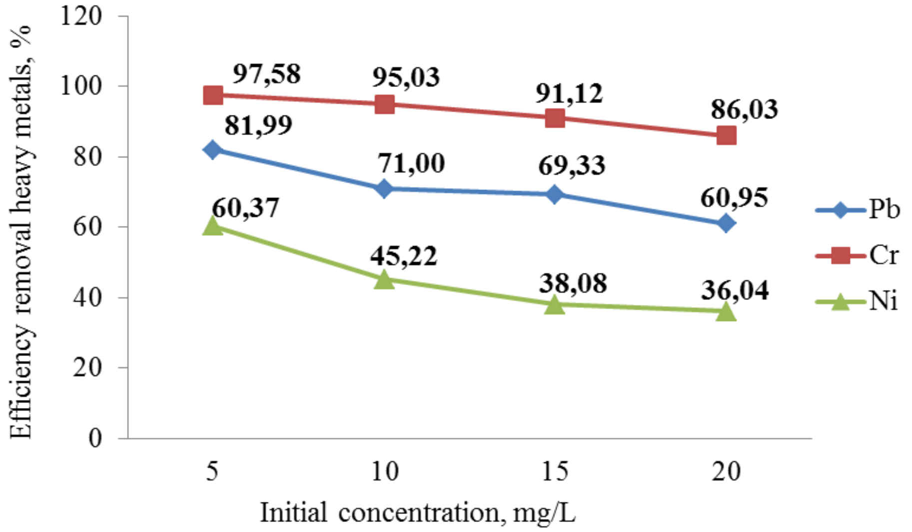

Fig4. Efficiency of removal of heavy metal ions Cr (III), Pb(II) and Ni(II) treated with thermally activated with H_2SO_4

Removal efficiencies of heavy metals ions Cr(III), Pb (II) and Ni(II) treated with HCl-activated Ca-bentonite

The highest removal efficiencies of 99.83%, 80.91%, and 71.81% for Cr(III), Pb(II) and Ni(II) were achieved at the lowest concentrations of these heavy metals, while at the highest concentrations the lowest removal efficiency: 96.30%, 48.50% and 36.65% for Cr(III), Pb(II) and Ni(II)

Based on the figures, as in the previous cases, it is clear that with increasing concentrations, the degree of efficiency of heavy metal ion removal decreased. The reason why this happens is that at one point Ca-bentonite is saturated with heavy metal ions. However, what still affects the obtained results is the mixing speed, which significantly affects the adsorption process. Ayari at all. (2007) obtained similar results in their study. They also investigated the influence of initial concentrations on the adsorption process. What was found is that with increasing concentrations, the adsorption capacity also increased, and the efficiency of heavy metal ion removal decreased [23].

One of the most commonly used adsorption isotherms to describe the adsorption process is the Freundlich adsorption isotherm. [24] The empirical model of this isotherm describes adsorption on a heterogeneous surface, where the constant Kf is a parameter related to the binding capacity of the adsorbate to the adsorbent and represents the adsorption strength, while the constant 1/n represents the surface heterogeneity factor. heterogeneity [25] [26].

Based on the data on the values of Freundlich isotherm given in the table, it can be concluded that the coefficient 1/n for all used biosorbents is less than one, which indicates that it is a large heterogeneous surface of used sorbents, ie that there are high energy sorption centers according to the examined heavy metal ions. The exception is the TAB for the adsorption of Ni(II) where this value is slightly higher than 1. The Kf constant values for all biosorbents used were about 10. For all analyzed biosorbents, the correlation factor (R^2) was 1, which further confirmed that the obtained values best describe the Freundlich adsorption model of the isotherm.

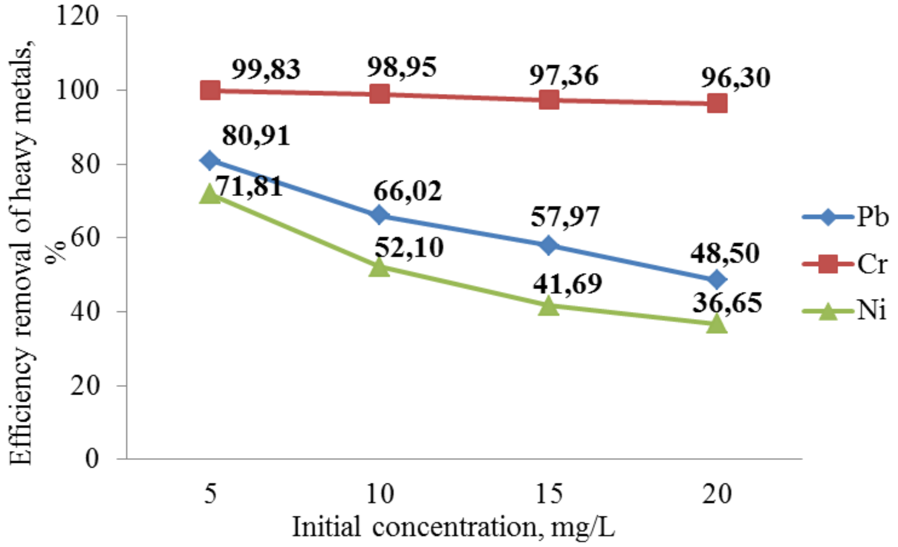

Fig.5. Heavy metal ion removal efficiencies Cr(III), Pb(II) and Ni(II) treated with Ca-bentonite activated HCl acid

***Values* of Freundlich constants**

Table 4. Values of Freundlich constants

Metal	Adsorbens	Kf	1/n	R^2
Pb(II)	NB	9,995396	0,9998	1
	TAB	9,993095	0,9997	1
	ABh	9,997698	0,999	1
	ABs	9,993095	0,9998	1
Cr(III)	NB	9,993095	0,9998	1
	TAB	9,995396	0,9998	1
	ABh	10	1	1
	ABs	9,993095	0,9998	1
Ni(II)	NB	9,995396	0,9998	1
	TAB	10,0023	1,0002	1
	ABh	9,997698	1	1
	ABs	10	1	1

Legend: NB – natural (raw) bentonite; TAB – thermal activated bentonite; ABh – acid activated bentonite with HCl; ABs – acid activated bentonite with H_2SO_4

IV. CONCLUSION

By applying natural, thermally and acid-activated Ca-bentonite, it is possible to remove Cr(III) Ni(II) and Pb (II) from the wastewater with a satisfactory degree of adsorption. The highest percentage of metal ion removal was achieved by removing Cr(III) with acid-activated bentonite with HCl and this percentage was 99.83% at a concentration of 20 mg/L. The highest percentage of Ni (II) removal was with the use of thermally activated bentonite and this percentage of removal was 84.24%. Natural bentonite proved to be the best for the removal of Pb(II) ions, and the percentage of removal was 96.03%. Cr(III) had a removal efficiency above 97% using natural, thermally and acid-activated Ca-bentonite, while Ni(II) had a removal efficiency of 60.37% for acid-activated bentonite with H_2SO_4 to 84.24% with thermally activated bentonite.

Based on the data on the values of Freundlich isotherm it can be concluded that the coefficient 1/n for all used biosorbentsis less than one, which indicates that it is a large heterogeneous surface of used sorbents, ie that there are high energy sorption centers according to the examined heavy metal ions.

Based on the obtained experimental results, it can be concluded that Ca-bentonite was used from the area of Šipovo, Bosnia and Herzegovina can be used to remove heavy metal ions.

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