

Removal of As(V) and Hg(II) ions from simulated wastewater using natural and modified Ca - bentonite

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Abstract— Using natural and modified Ca-bentonite as an adsorbent to observe a satisfactory trend in the removal of heavy metal ions As(V) and Hg(II) from simulated wastewaters. In this original scientific paper, Ca-bentonite was modified in two ways, thermally activated at a temperature of 300 °C for 3 hours and acid activated with HCl and H₂SO₄, molar concentrations 0,4 mol/L. Ca-bentonite used in this original scientific work was used from the Šipovo mine (Šipovo mine), Bosnia and Herzegovina and proved to be an excellent bioadsorbent for the removal of present ions from simulated wastewaters. Also this is eco-friendly adsorbent and low costed compared to other expensive adsorbents. Due to its chemical composition in which two oxides predominate, namely SiO₂ (48.28 mass %) and Al₂O₃ (23.04 mass%), it can be concluded that Ca-bentonite from the Šipovo mine (Šipovo mine), Bosnia and Herzegovina belongs to the group of refractory materials. The highest removal efficiency of As(V) ions expressed in % was 75.11 at the initial concentration of 1.5 mg/L and was recorded using HCl acid-activated Ca-bentonite. The efficiency of Hg(II) ion removal was the highest using thermally activated Ca-bentonite and this value was 99.66% at an initial concentration of 1 mg/L.

Keywords— Ca-bentonite, eco-friendly adsorbent, heavy metals, removal, wastewater

I. INTRODUCTION

Environmental pollution by heavy metals has raised considerable attention due to their toxic impacts on plants, animals and human beings [1]. These pollutants affect all groups of organisms and ecosystem processes, including microbial activities [2]. Living systems most often interact with a cocktail of heavy metals in the environment [3].

Heavy metals are natural constituents of the environment, but indiscriminate use for human purposes has altered their geochemical cycles and biochemical balance [4]. The biggest increase is the pollution of the environment with wastewater from industry, which results in a reduction of drinking water for humans and animals [5]. Heavy metals are well-known environmental pollutants due to their toxicity, persistence in the environment, and

bioaccumulative nature [6]. These inorganic pollutants are being discarded in our waters, soils and into the atmosphere due to the rapidly growing agriculture and metal industries, improper waste disposal, fertilizers and pesticides [7]. Heavy metal pollution has become a growing concern today and poses a serious threat to humans and animals [8]. Metals tend to accumulate in water and move up through the food chain [9]. The toxicity of heavy metals mainly depends on their relative oxidation state, which is responsible for physiological biotoxic effects. When these metals enter living organisms, they, in combination with proteins, enzymes and DNA molecules, form highly stable biotoxic compounds, thus altering their proper functioning and interfering with their bioreactions [10]. They are classified as trace elements because of their presence in trace concentrations in various environmental matrices [11a]. Major contaminating sources of As(V) are herbicides, cattle and sheep dips and insecticides. Also as a desiccant for cotton crop to facilitate the mechanical harvesting of the crop. The availability of Hg(II) in wastewater comes from based fungicides, sewerage sludge and atmospheric fall out resulting from combustion of fossil fuels and industrial processes [11b]. With the development of researches, the treatments of wastewater have reached a certain level. Whereas, heavy metals in wastewater cause special concern in recent times due to their recalcitrance and persistence in the environment [12].

Thus, the main strategies of pollution control are to reduce the bioavailability, mobility, and toxicity of metals [13]. Today, there are many conventional methods for removing heavy metal ions from wastewater. Removal of heavy metals from industrial wastewaters can be accomplished through various treatment options, including such unit operations as chemical precipitation, coagulation, complexation, adsorption, ion exchange, solvent extraction, foam flotation, electro-deposition, cementation, and membrane operations [14]. Common methods for removing heavy metals have numerous drawbacks, including low efficiency, high costs, limited capacity and difficulties in spontaneously removing multiple heavy metals [15].

Adsorption is a process in which pollutants are adsorbed on the solid surface [16]. Due to the high uptake capacity and very cost-effective source of the raw material, sorption is a progression towards a perspective method [17]. Bentonite is absorbent aluminium phyllosilicate clay [18]. The relatively low cost and wide versatility of reactive barriers favour the use of bentonite as an important component in barrier systems [19]. Removal of heavy metal ions using bentonite is a profitable technique because the material is available, cheap compared to activated carbon and some other expensive adsorbents

[20]. Apkomie and Dawodua, 2015 reported that using bentonite it is possible to remove Ni(II) and Mn(II) ions from aqueous solutions above 90% [21].

II. METHODS

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

X-ray fluorescence was used to determine the elemental composition of natural Ca-bentonite, which is a standard method according to BAS EN 15309:2010. This method is used to determine the following elements: Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Br, Rb, Sr, Y, Zr, Nb, Mo, Ag, Cd, Sn, Sb, Te, I, Cs, Ba, Ta, W, Hg, Tl, Pb, Bi, Th and U. The accuracy of the method depends from the type of instrument and the element that is determined and ranges from 0.0001% to 100%.

Determination of heavy metal content in Ca-bentonite

The standard method (ISO 11047:1998, IDT) QMS-UP-68 was used to determine the content of heavy metal ions in Ca-bentonite.

Determination of pH of Ca-bentonite

The pH value of Ca-bentonite was determined by the standard method, (ISO 10390:2005, IDT), QMS-UP-66.

Determining the point of zero charge

The pH value of the point of zero charge represents the state of the surface of the material when the sum of the negative charges is equal to the sum of the positive charges. This quantity is determined based on the change in the pH solution of the corresponding electrolyte under the influence of the adsorbent.

NaNO₃ concentration 0.1 mol/L, volume 50 mL was used as the basic electrolyte, which adjusted the pH value in the interval from 2-10 by adding HNO₃ or NaOH (0.01/0.1 mol/L). The initial pH value was measured and labeled as pH_i. After that, Ca-bentonite was added and the suspension was left to stand for 24 hours with occasional stirring, the pH value was measured and marked as pH_f. Based on the measured values, the diagram pH_f = f(pH_i) is created.

Thermal activation of Ca-bentonite

Thermal activation of Ca-bentonite was carried out by heating 25 grams of natural Ca-bentonite at a temperature of 300 °C for three hours. As a result of annealing, thermally activated Ca-bentonite was obtained, which was used as an adsorbent for the removal of As(V) and Hg(II) ions from simulated wastewater.

Acid activation of Ca-bentonite

Acidic activation of Ca-bentonite was performed using two acids, namely HCl and H₂SO₄, which are in molar concentrations of 0.4 mol/L. The acid activation process was carefully carried out by gradually adding HCl acid in a total volume of 400 mL to 30 g of natural Ca-bentonite and mixing was carried out for the next 8 hours at 200 rpm. After that, the sample was filtered, dried at a temperature of 105 °C and sieved through a sieve with a diameter of 75 µm. The same procedure was done with H₂SO₄ acid. This acid-activated Ca-bentonite with HCl and H₂SO₄ was used as an adsorbent for the removal of As(V) and Hg(II) ions from simulated wastewater.

Preparation of synthetic solutions of heavy metal ions

Synthetic aqueous solutions of As(V) is prepared from the atomic absorption standard (AAS) of 1000 µg/mL in 1 mol/L HNO₃. It is produced from a very pure metal or salt (at least 99.99%) and tested with an ISO 17025 accredited test method (INAB Ref: 264T). Synthetic aqueous solutions of Hg(II) is prepared also from the atomic absorption standard (AAS) of 1000 µg/mL in 1 mol/L of HNO₃. Table 1. shows the initial concentrations (mg/L) of As(V) and Hg(II) ions which simulating wastewater.

Table 1. Initial concentrations of heavy metals

Metals	(mg/L)	(mg/L)	(mg/L)	(mg/L)
As(V)	0,5	1	1,5	2
Hg(II)	0,5	1	1,5	2

Heavy metal ions adsorption process

The process of adsorption of heavy metal ions As(V) and Hg(II) from aqueous solutions in this original scientific work was carried out using the following pre-prepared adsorbents:

1. natural (raw) Ca-bentonite,
2. thermally activated Ca-bentonite,
3. acid-activated Ca-bentonite with 0.4 mol/L HCl,
4. acid-activated Ca-bentonite with 0.4 mol/L H₂SO₄.

A mass of 1 g of natural Ca-bentonite was weighed on an analytical balance, which was then added to Erlenmeyer flasks of 250 mL containing prepared stock solutions of heavy metal ions As(V) and Hg(II) in different concentration intervals that were prepared in advance. The Erlenmeyer flasks were placed under continuous stirring for six hours at room temperature and a speed of 125 rpm. After the sample mixing process, slow filtration was performed through blue filter paper. In the resulting filtrate, the residual concentration of As(V) and Hg(II) was

then determined by atomic absorption spectrophotometry. The same process of adsorption of heavy metal ions As(V) and Hg(II) from aqueous solutions was repeated for all four aforementioned adsorbents.

Determination of heavy metal content by atomic absorption spectrophotometry

The residual concentration of heavy metal ions As(V) and Hg(II) expressed in mg/L after the adsorption process was determined using an atomic absorption spectrophotometer, 240 Series Agilent Technology. The mathematical equation that was used to calculate the percentage efficiency of removal of heavy metal ions in wastewater is:

$$\% = C_r - C_i / C_i$$

where is:

% - percentage efficiency of removal of heavy metal ions

C_i – initial concentration of heavy metal ions (mg/L)

C_r – residual concentration of heavy metal ions (mg/L)

III. RESULTS AND DISCUSSION

Results of determination of the basic composition of natural (raw) Ca-bentonite by X-ray fluorescence

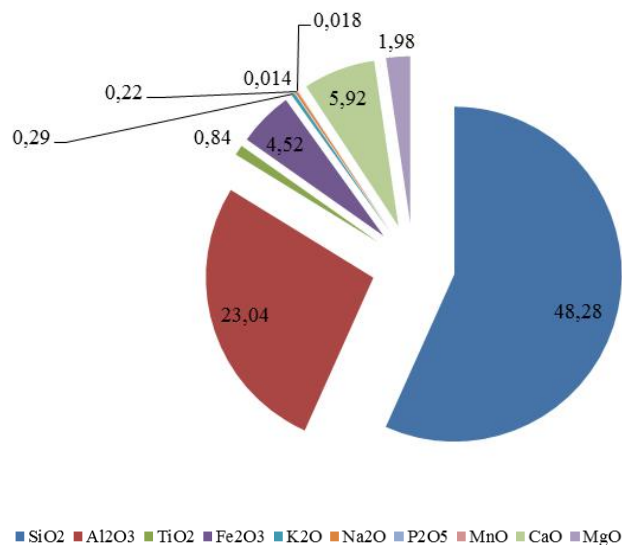


Fig.1. Chemical composition of analyzed natural Ca-bentonite by X-ray fluorescence expressed in mass percentage (mass %)

Based on Figure 1., which shows the elemental composition of natural Ca-bentonite expressed in mass percentages %, it can be seen that the highest proportion of SiO₂ oxide is 48.28 mass % and Al₂O₃ oxide is 23.04 mass %. In addition to these two most abundant oxides, others were also recorded in smaller percentages, which is clearly visible in Figure 1.

Similar results were obtained by other scientists such as Abdullahi and Audu, 2015 who compared two samples of natural bentonite, and their results were as follows: 48.16% and 49.87% for SiO₂, 14.86 and 14.98% for Al₂O₃ and Fe₂O₃, respectively: 4.80% and 5.12%. [22]. Further, comparing the SiO₂ oxide results with the results reported by Newke et al., 2008 (45 mass%) and Tabak et al., 2015 (48.35%) to conclude that it is a material that is a significant carrier of aluminosilicate [23], [24]. Based on these obtained results, it can be concluded that Ca-bentonite from the Shipovo mine (Šipovo mine), Bosnia and Herzegovina belongs to the group of refractory materials.

Results of determination of heavy metal content in natural Ca-bentonite

The content of heavy metals in the bentonite clay sample is showed in Table 2.

Table 2. Content of heavy metals in natural Ca-bentonite

Elements in Ca-bentonite	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 2.). 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 [25a]

Results of determination of pH value of Ca-bentonite

The measured pH value of natural Ca bentonite was 8.86.

Results of determining the zero charge point

The zero charge point determined for Ca-bentonite is shown in the Figure 2. 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 [25b].

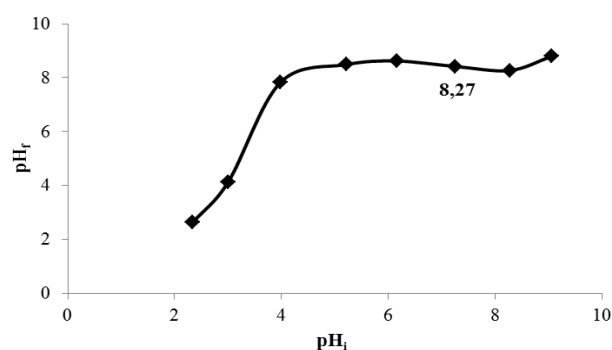


Fig.2. Zero charge point

Results of determining the optimal adsorption capacity
Removal As(V) and Hg(II) ions from simulated wastewater treated with natural Ca-bentonite

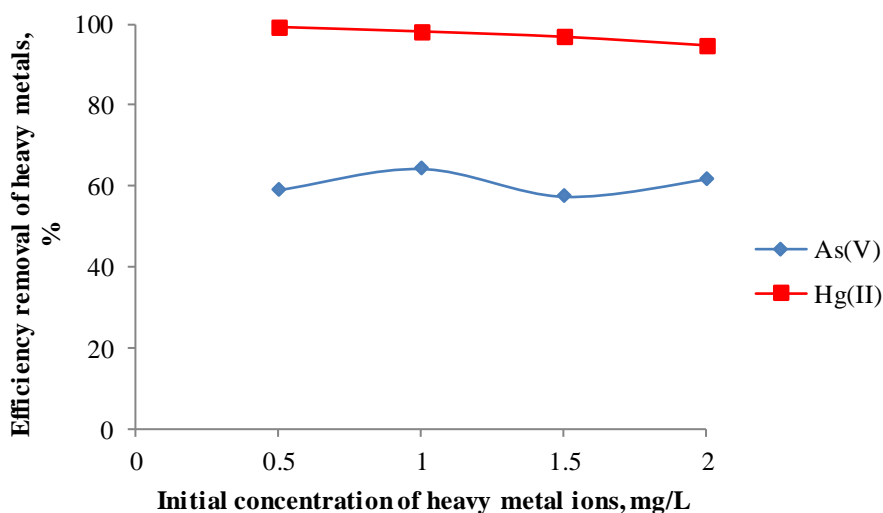


Fig.3. Removal efficiency of As(V) and Hg(II) ions from simulated wastewater treated with natural Ca-bentonite

Based on Figure 3., it can be clearly seen that the highest removal percentage of As(V) ions was at the initial concentration of this metal ion of 1 mg/L, and this removal percentage was 64.31%. However, the percentage of removal of Hg(II) ions was above 94% at all concentrations. The highest percentage of Hg(II) ion removal is observed at the lowest initial concentration of this metal ion. By increasing the initial concentration of the metal ion Hg(II), the percentage of removal also

decreased. Accordingly, the lowest removal percentage was at the highest initial concentration and was 94.85%. Viraraghavan and Kapoor, 1994 reported that the percent removal of Hg(II) ions from wastewater with the application of Na-bentonite amounted to 34.2% [26]. Based on this, it can be concluded that Ca-bentonite showed a significantly higher adsorption capacity for the removal of Hg(II) ions compared to Na-bentonite, and that it is a high-quality adsorption material.

Removal As(V) and Hg(II) ions from simulated wastewater treated with thermally activated Ca-bentonite

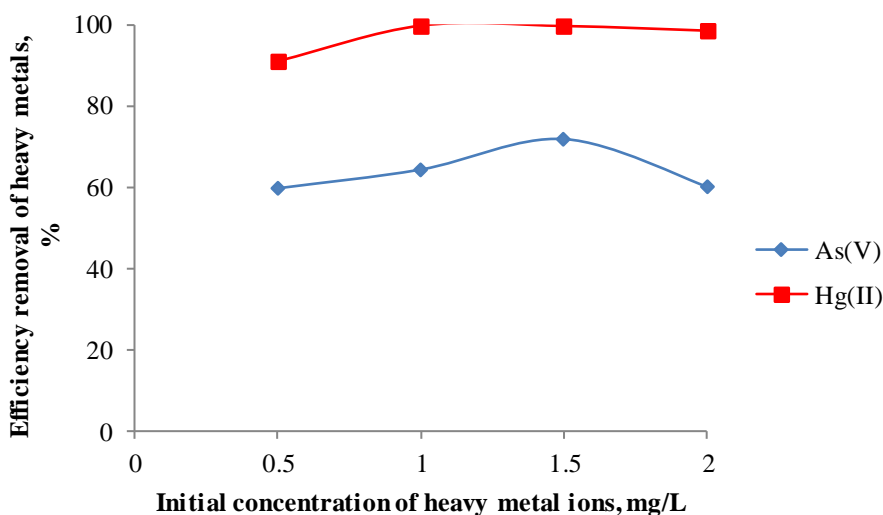


Fig.4. Removal efficiency of As(V) and Hg(II) ions from simulated wastewater treated with thermally activated Ca-bentonite

The removal efficiency of As(V) and Hg(II) ions using thermally activated Ca-bentonite had a similar removal

curve as when using natural Ca-bentonite. The highest removal percentage of As(V) ions was 71.82% at the

initial concentration of 1.5 mg/L, and after this value, the removal percentage decreased. At the initial concentration of 0.5 mg/L, less Hg(II) ions were removed than when using natural Ca-bentonite. However, the highest percentage of Hg(II) ion removal was 99.66% at the initial

concentration of 1 mg/L, which is a higher value compared to the application of natural Ca-bentonite. After that, the trend of decreasing removal percentage continued.

Removal As(V) and Hg(II) ions from simulated wastewater treated with H₂SO₄ activated Ca- bentonite

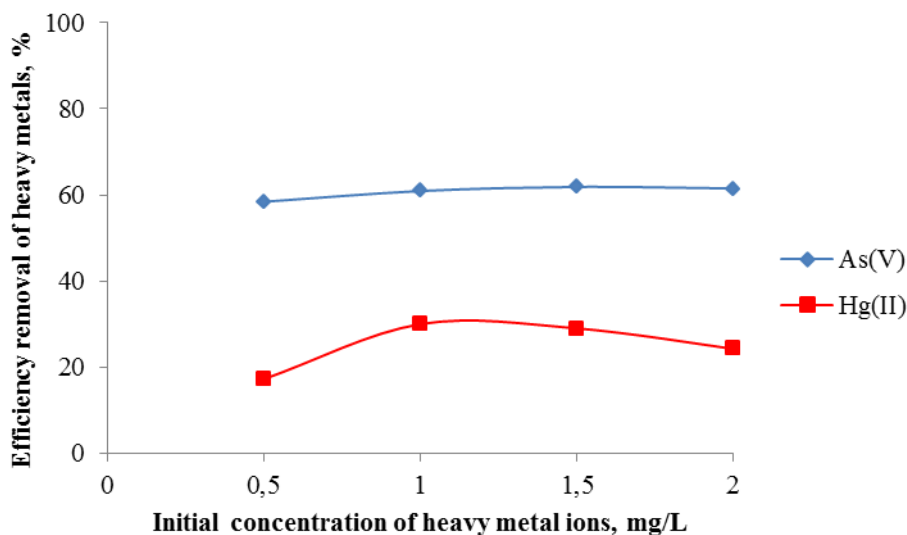


Fig.5. Removal efficiency of As(V) and Hg(II) ions from simulated wastewater treated with H₂SO₄ activated Ca- bentonite

As can be seen from Figure 5., the percentage of removal of As(V) ions is higher in relation to Hg(II) ions using Ca-bentonite activated with H₂SO₄ compared to the removal using natural Ca-bentonite and thermally activated Ca-bentonite. The highest percentage of removal of Hg(II) ions was 30 mg/L at an initial concentration of 1 mg/L, while with further increase of the initial concentration, a trend of decreasing percentage of removal of these ions

was observed. The percentage removal of As(V) ions had similar values to the percentage removal of these ions using natural Ca-bentonite and thermally activated Ca-bentonite. As with Hg(II) and As(V), a trend of increased removal percentage was observed and the highest value was recorded at an initial concentration of 1.5 mg/L and was 61.75%, while already at an initial concentration of 2 mg /L observed a decrease in the removal percentage of these ions.

Removal As(V) and Hg(II) ions from simulated wastewater treated with HCl activated Ca-bentonite

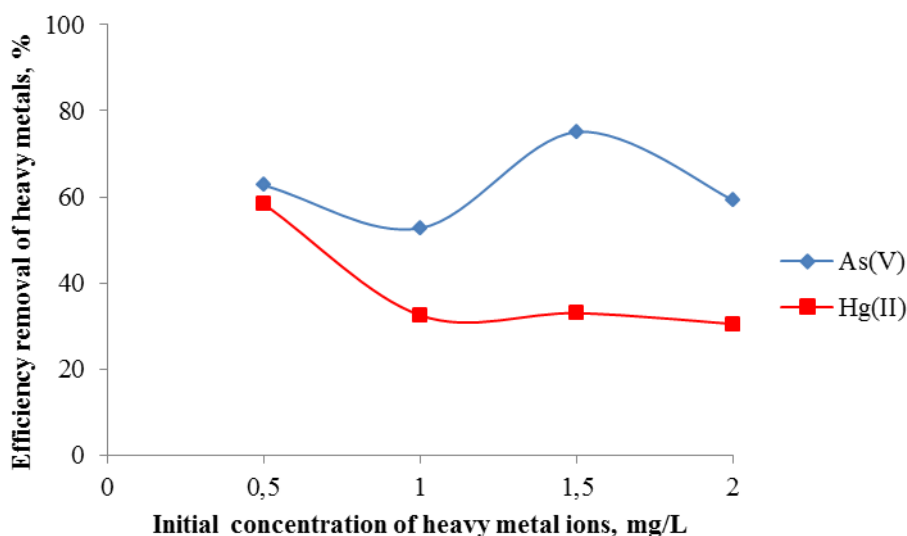


Fig.6. Removal efficiency of As(V) and Hg(II) ions from simulated wastewater treated with HCl activated Ca- bentonite

The removal efficiency of As(V) ions using Ca-bentonite activated with HCl was 75.11% at an initial concentration of 1.5 mg/L, and this is the highest recorded value in relation to the adsorption procedures used so far. A slightly lower percentage of removal was recorded using Ca-bentonite activated with H₂SO₄. From this it can be concluded that Ca-bentonite activated with HCl is the best choice compared to natural, thermally and acid-activated Ca-bentonite with H₂SO₄ for removal of As(V) ions from simulated wastewater. Application of acid activated Ca-bentonite with HCl and H₂SO₄ in both cases better removal of As(V) ions compared to Hg(II) ions. The highest percentage of removal of Hg(II) ions was 58.40% at the initial concentration of 0.5 mg/L, while with further increase of the initial concentration, a constant trend of decreasing percentage of removal of these ions was observed.

Values of Freundlich constants

Table 4. Values of Freundlich constants

Metal ions	Adsorbens			
		Kf	1/n	R ²
As(V)	NB	10	1	1
	TAB	10	1,0001	1
	ABh	10	0,9995	1
	ABs	10	1	1
Hg(II)	NB	10	1	1
	TAB	10	1	1
	ABh	10	-	1
	ABs	10	-	1

Legend: NB – natural (raw) bentonite; TAB – thermal activated bentonite; ABh – acid activated bentonite with HCl; ABs – acid activated bentonite with H₂SO₄

Based on the data on the Freundlich isotherm values 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 the used sorbents, i.e. that there are sorption centers with high energy that show good sorption intensity according to the investigated heavy metal ions. The exception is TAB for the adsorption of As(V) ions, where this value is slightly higher than 1. The values of the Kf constant for all used biosorbents were around 10. For all analyzed biosorbents, the correlation factor (R²) was 1, which additionally confirmed that the obtained values is best described by the Freundlich adsorption isotherm model. The isotherm for the adsorption of the heavy metal ions on bentonite clay was

confirmed by the Freundlich isotherm which offered good consequences. The results indicated that bentonite was utilized as an efficient ion exchange element for the removal of heavy metal ions from polluted water [27].

IV. CONCLUSION

Based on the conducted experiment, it can be concluded that modified, ie thermally activated and HCl and H₂SO₄ acid-activated Ca-bentonite gives better results in removing As(V) and Hg(II) ions compared to natural (raw) Ca-bentonite. Natural Ca-bentonite also had an enviable removal percentage of Hg(II) ions and this value was above 94% for all initial concentrations of this metal ion. However, a slightly higher percentage was nevertheless thermally activated by the application of Ca-bentonite. Also, a solid percentage of As(V) ion removal was recorded using natural Ca-bentonite, however, the best result was HCl acid-activated Ca-bentonite, whose removal percentage was 75.11%. 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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