

Biosorption of Lead (II) by Natural Bentonite: Adsorbent Characterization and Performance Assessment

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ABSTRACT

In this research, the results of bentonite characterization (pH value of bentonite suspension, point of zero charge, cation exchange capacity, SEM, XRF, DTG) are presented. The results of lead (II) removal efficiency at initial lead (II) concentrations of 200, 300 and 400 mg/L, and biosorbent dosage of 1 gram in 50 ml of lead (II) solution, are also presented, as well as the values of the Freundlich and Langmuir constants from the Freundlich and Langmuir adsorption isotherms. The obtained results showed that removal efficiency is high for all three examined initial lead (II) concentrations, and it is above 99%. The lead (II) removal efficiency slightly decreases with an increase in initial lead concentration. Experimental data obtained from adsorption experiment with contact time of 2.5 minutes, stirring rate 100 rpm, temperature 25°C and pH value 5 are better fitted with the linearized Langmuir equation isotherm, giving an R^2 value closest to unity (0.9994), than to linearized Freundlich equation (0.9886).

Keywords- biosorption, bentonite, characterization, lead, isotherm.

The main sources of heavy metal pollutants are mining, metallurgy, machinery manufacturing, electroplating, chemical industry, pesticide, paint, fuel, etc. [1]. Heavy metals such as lead, mercury, arsenic, copper, zinc and cadmium are highly toxic when adsorbed into the body. Lead, one of the earliest metals recognized and used by humans, has a long history of beneficial use to humankind, but now been recognized as toxic and as posing a widespread threat to humans [3]. Of particular concern for the general population is the effect of lead on the central nervous system. Lead has been shown to have effects on hemoglobin synthesis and anemia. Lead is known to cause kidney damage. Some of the effects are reversible, whereas chronic exposure to high lead levels may result in continued decreased kidney function and possible renal failure [4].

The traditional methods to remove the heavy metals from aqueous environment include precipitation, filtration, ion exchange, evaporation, reverse osmosis, solvent extraction, adsorption, electrochemical treatment and membrane technologies. However, these traditional methods are either inefficient or expensive when heavy metals exist in lower concentrations. Consequently, it is essential to find new methods for effective removal of heavy metals from water and wastewater [5]. Adsorption is one of the most preferred methods among these techniques because it has many advantages, such as high efficiency, easy handling, and low cost. The selection of adsorbents is an important research topic in the application of adsorption techniques. In this regard, various adsorbents have been studied for the wastewater treatment, including conventional materials (e.g., active carbon, silica gel) and nonconventional adsorbents (e.g., biosorbents, nanomaterials). Interest in biosorption for the removal of heavy metals is growing because of its excellent efficiency, minimization of secondary waste, and low cost of biosorbent materials [1].

Biosorption is a process that utilizes inexpensive biomass or natural materials to sequester toxic heavy

I. INTRODUCTION

Nowadays, human activities have caused serious environmental pollution, and water pollution is one of the most important problems worldwide [1]. Industries are using different type of chemicals as a part of their manufacturing process. Effluents released from industries contain chemical pollutants. These pollutants may be organic or inorganic in nature. Waste water polluted with organic pollutants is easy to purify as they are biodegradable. However, waste water polluted with inorganic pollutants is difficult to treat as they are non-biodegradable and therefore they will remain in the environment. These pollutants are known as heavy metals and dyes [2].

metals and is particularly useful for the removal of trace levels of contaminants from industrial effluents [6]. Biosorption is considered to be a fast physical/chemical process, and its rate is governed by the type of the process. In another sense, it can also be defined as a collective term for a number of passive accumulation processes which in any particular case may include ion exchange, coordination, complexation, chelation, adsorption and microprecipitation [7].

The main objective of this research is to determine the possibility of using natural bentonite from deposit Šipovo in Bosnia and Herzegovina for removal of lead (II) from aqueous solution.

Previously, the removal of lead (II) by using natural bentonite from different deposits has been investigated [2, 3, 8, 9]. Khan M. R., et al 2015 [2] claim that bentonite clay from Bhawnagar area can successfully be utilized for lead removal from aqueous solution, and that adsorption is a spontaneous phenomenon. D. John Babu et al 2012 [3] studied the removal of lead (II) from aqueous solutions on to the Bentonite clay from ONGC Rajahmundry by using batch adsorption techniques. The results of this study demonstrated that the bentonite clay constituted a promising material for the development of a low cost biosorption technology for the removal of lead (II) from wastewaters. Jock Asanja Alexander et al 2018 [8] used Bentonite clay from Dijah-Monkin town, Taraba state of Nigeria for research, and presented the results on which they concluded that the natural bentonite can be readily used for the treatment of wastewater containing lead (II) with little cost implications. Saad A. Al-Jilil 2015 [9] made a conclusion that natural Bentonite clay from West of Saudi Arabia is economically attractive proposition for the adsorption of lead (II) from wastewater.

The results of bentonite characterization (pH value of bentonite suspension, point of zero charge, cation exchange capacity, SEM, XRF, DTG) are presented in this paper. The results of lead (II) removal efficiency at initial lead (II) concentrations of 200, 300 and 400 mg/L, and biosorbent concentration of 1 gram, are also presented, as well as the calculated values of the Freundlich and Langmuir constants from the Freundlich and Langmuir adsorption isotherms.

II. MATERIAL AND METHODS

2.1. Adsorbent characterization

Natural bentonite from deposit Šipovo in Bosnia and Herzegovina was used as biosorbent for lead (II) removal from aqueous solution. Before adsorption experiments, adsorbent characterization was done by determination of pH value of bentonite suspension, point of zero charge, cation exchange capacity, and by using SEM, XRF, DTG analysis.

2.1.1. pH value of bentonite suspension, Point of zero charge, Cation exchange capacity

When a certain amount of biosorbent is added to distilled water, which is pH neutral, the pH value of the medium changes due to the influence of the acid-base nature of the suspended material. The pH value of the sorbent suspension in water is an indicator of the overall dominance of acidic, i.e., basic functional groups on the surface of the solid phase. To determine the pH value of the suspension, 0.2 grams of bentonite was suspended in 30 cm³ of distilled water and occasionally stirred in a closed PVC container for 72 hours, after which the pH was measured.

The point of zero charge (pH_{pzc}) is defined as the pH value of the suspension at which the total charge on the adsorbent surface is zero [10]. To determine pH_{pzc}, a series of 0.1 M KNO₃ solutions with different initial values for pH (pH 2, pH 3, pH 4, pH 5, pH 6, pH 7, pH 8, pH 9 and pH 10) were made, which were adjusted by using 0.01 M HNO₃ solution and 0.1 M NaOH solution. 50 cm³ of prepared solutions was poured to polyethylene bottles with a cap. The solutions were stirred for 1 minute at 1000 rpm, and the pH values were measured again and marked as pH_{initial}. Then 0.2 g of bentonite was added to each of these solutions and the suspensions were left for a period of 24 hours with occasional shaking. After 24 h, the pH values of the solutions were measured again and marked as the pH_{final}.

The main mineral component of bentonite is montmorillonite. Thus, the montmorillonite's properties predominate the bentonite's characteristic. Cation's exchange is one of the important characters in montmorillonite. Metal cations adsorbed on montmorillonite crystalloid interlayer are exchangeable, so they can exchange with the similar electric property and the same electric quantity in solution. The exchange and the adsorption are reversible. Montmorillonite's ions exchange is mainly cation exchange [11]. For Cation exchange capacity (CEC) determination, bentonite is converted to the Ca²⁺ form by treatment with saturated Ca(OH)₂ solution. There is an exchange of ions from bentonite with Ca²⁺ ions. The amount of calcium, before and after the change, is determined complexometrically. The bentonite sample is dried for one hour at 105 °C before testing. 1 g of dried bentonite is placed in a glass vial and 50.0 mL of saturated calcium solution is added with a graduated pipette. It is closed with a rubber stopper and stirred at 30 °C for 24 h. After 24 hours, the solution was filtered through filter paper (white tape) and the precipitate was washed with alcohol. Then distilled water is added up to the mark. The concentration of residual calcium ions in the solution is determined. The concentration of calcium ions in the saturated solution as well as in the test solution is determined by pipetting 5.0 mL of the solution into an Erlenmeyer flask, diluting with water to 25 mL, adding 5 mL of triethanolamine,

dropwise 20% KOH to pH 12. The murexide indicator was then added and titrated with EDTA solution ($c = 0.01$ M) until the color transition.

2.1.2. SEM analysis

Determination of morphological properties of bentonite, before and after adsorption process, was performed by scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDS), using JEOL JSM 6420 LV scanning electron microscope, with an acceleration voltage of 20 kV. The sample was coated with a 15 nm layer of gold, with a density of 19,32 g/cm³.

2.1.3. XRF analysis

Chemical composition (in the form of oxides) of bentonite was determined by fluorescent X-ray analysis, using Bruker S8 TIGER, with characteristics: X-ray tube operating voltage of 60 kV, maximum current of 170 mA and maximum X-ray tube power of 4 kW.

2.1.4. DTG analysis

The content of absorbed moisture and hydroxyl groups was determined by DTG analysis, using a Q600 thermal analyzer (TA Instruments, New Castle, DE, USA). The analysis was performed in a corundum tank, under a nitrogen atmosphere at a flow rate of 100 mL/min and at a heating rate of 20 °C/min. The weight of the sample is 3 mg. The reference sample is an empty corundum tank. The temperature interval of the analysis is from room temperature to 1000 °C.

2.2. Adsorption experiment

Batch adsorption experiments were carried out by shaking 1 gram of bentonite with 50 ml solution of lead (II) for 2.5 minutes at 100 rpm on magnetic stirrer. Adsorption studies were carried out at temperature of 25 °C, pH value of 5, with initial lead (II) concentrations of 200, 300 and 400 mg/L. Solutions of required concentrations are prepared by diluting the lead (II) standard solution (Pb (NO₃)₂ in HNO₃ 0.5 mol/l) with concentration of 1000 mg/L lead (II) ions. pH adjustment was carried out using the hydraulic acid (HCl) and sodium hydroxide (NaOH) with concentration range from 0.01 to 0.1M. All analytical grade chemicals used were commercially obtained.

After shaking for 2.5 minutes of contact time, the samples were filtered through double Blue Ribbon Filter – Grade 589/3: 2 μm, ashless standard filter paper by using vacuum pump. The concentration of residual lead (II) was determined by an atomic absorption spectrophotometer (Perkin Elmer 3110).

2.2.1. Removal efficiency

Based on the results of the residual lead (II) concentration after adsorption process, removal efficiency is calculated by using equation [12]:

$$\text{Removal efficiency (\%)} = \frac{C_i - C_f}{C_i} \times 100 \quad (1)$$

where C_i and C_f are the concentration of lead (II) before and after adsorption, respectively (mg/l).

2.2.2. Adsorption isotherms

The mechanisms and intensity of adsorption were described by the use of two common adsorption models: Freundlich and Langmuir adsorption isotherms. These models describe adsorption processes on a heterogeneous or homogenous surface, respectively. The Freundlich adsorption isotherm describes the multilayer adsorption by heterogeneous surface [13]. Freundlich isotherm is capable of describing the adsorption of organic and inorganic compounds on a wide variety of adsorbents including biosorbent. The Freundlich equation, in the linear form is written as [7]:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (2)$$

where q_e is the amount of lead (II) adsorbed per unit weight of adsorbent (mg/g bentonite), C_e is the equilibrium concentration of lead (II) (mg/l), K_F (mg/g) and n are the constant characteristics of the system.

The amount of lead (II) adsorbed per unit weight of adsorbent is calculated by using equation [12]:

$$q_e = \frac{(C_i - C_f) \times V}{W} \quad (3)$$

where V (l) is the volume of lead (II) solution, and W (g) is the dosage of bentonite.

The Langmuir isotherm is valid for monolayer sorption due to a surface with finite number of identical sites [13], and only can accommodate one adsorbed atom and the ability of a molecule to be adsorbed on a given site is independent of its neighboring sites occupancy. The Langmuir equation, in the linear form is written as [7]:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{K_L q_{max}} \quad (4)$$

where q_{max} is the maximum adsorption capacity (mg/g), and K_L is the adsorption equilibrium constant (l/mg).

III. RESULTS AND DISCUSSION

3.1. Adsorbent characterization

3.1.1. pH value of bentonite suspension, Point of zero charge, Cation exchange capacity

Determined pH value of suspension is 9.7 and that is an indicator of the overall dominance of basic functional groups on the surface of the bentonite.

pHpzc is determined graphically as the point of intersection of the obtained curve with x axis on the graph of the dependence $\text{pH}_{\text{initial}} - \text{pH}_{\text{final}}$ of $\text{pH}_{\text{initial}}$, shown in Fig. 1.

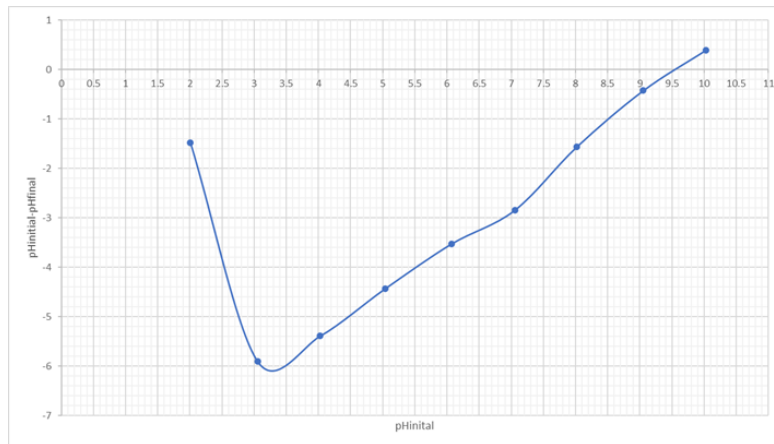


Fig.1. Graph of the dependence $pH_{initial} - pH_{final}$ of $pH_{initial}$

As shown in Figure 1, the determined value for the pH_{pzc} of the bentonite is 9.5. At this pH value, the amount of positively charged centers on the adsorbent surface is equal to the amount of negatively charged centers. The zero charge point is used to understand the mechanism of the adsorption process for different pH values. In fact, pH_{pzc} indicates the electrostatic interactions that occur between the adsorbent surface and the adsorbate. If $pH > pH_{pzc}$ the adsorbent surface is negatively charged, while at $pH < pH_{pzc}$ the adsorbent surface is positively charged [10]. The obtained pH_{pzc} value is in accordance with the obtained result for pH of the suspension, that the adsorbent contains more basic functional groups.

One of the mechanisms that can participate in the process of removing metal ions is ion exchange. In this regard, in order to examine the affinity of the adsorbent for ion exchange, the cation exchange capacity was determined. Cation exchange capacity for 1 gram of bentonite is calculated using equation:

$$CEC = \frac{A_0 - A_1}{A_0} \quad (5)$$

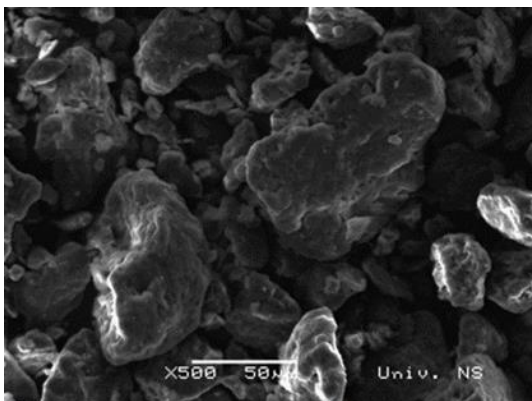
where A_0 is amount (mmol) of Ca^{2+} ions in 50 ml of saturated calcium solution, and A_1 is amount (mmol) of Ca^{2+} ions in 50 ml of calcium solution after stirring 1 gram of bentonite at 30 °C for 24 h.

Determined CEC for 1 gram of bentonite is 0.85 mmol Ca^{2+} , and for 100 grams of bentonite is 85 mmol Ca^{2+} , which is most often used. This value of CEC confirms that used natural bentonite is a type of clay mostly consists of the mineral montmorillonite [8, 14, 15, 16]. Montmorillonite mineral is characterized by the presence of exchangeable cations (Na, Ca, and Mg) [17].

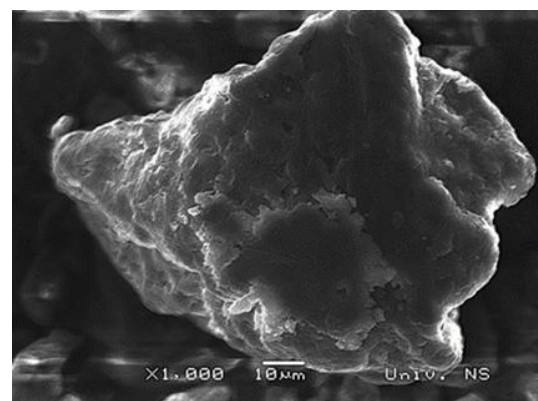
3.1.2. SEM analysis

Most micrographs of samples obtained by the SEM method are taken at a certain angle, which makes it seem as if the adsorbents do not have any pores. The presence of macropores is important because it facilitates the movement of liquid through the structure of the adsorbent and so facilitates the internal diffusion of the adsorbate, which is otherwise slow and represents a limiting grade of the adsorption process since mixing and convection have no effect.

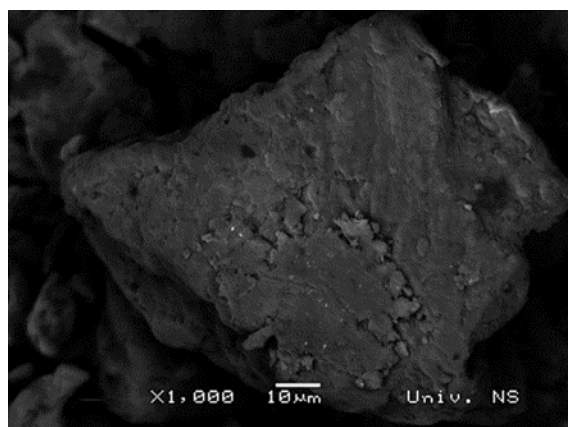
At a magnification of 1000x, a "fine powder" can be observed on the surface of the particle, which indicates that there is a developed porous structure in the structure of the particles. Gaps in the material can be seen in some parts of the image, which indicate that the structure of the analyzed particles is chaotic and irregular, which gives space for a lot of empty space in the structure. As magnification increases, particles of similar chaotic shape but much smaller in size can be seen on SEM images.



a)



b)

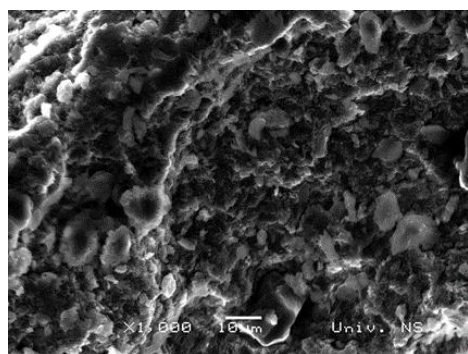


c)

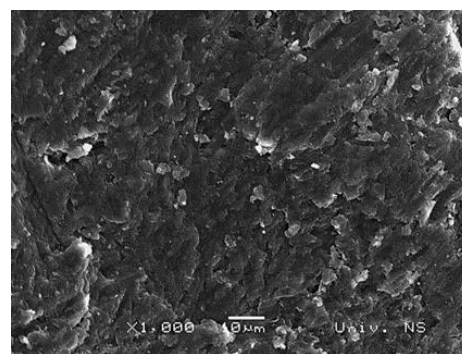
Fig 2. SEM images of bentonite before adsorption a) magnified 500x b) magnified 1000x c) magnified 1000x

Based on the SEM images it can be concluded that the structure of the adsorbent before and after the adsorption process is slightly changed. At a magnification of 1000x, an attempt was made to observe whether and to what extent the adsorption of Pb^{2+} ions from the solution influenced the change in the structure of bentonite. By comparing images of the bentonite surface before and after adsorption of lead cations, no significant differences in porosity can be observed. The presented bentonite particles on the SEM images after adsorption, as well as the particles before adsorption, show an irregular shape, chaotic structure as well as fine powder of smaller

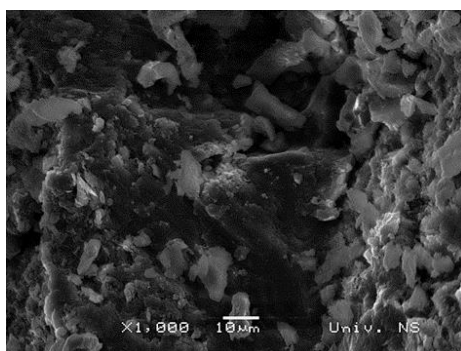
particles scattered on the surface of larger particles. Many scientific papers use scanning electron microscopy to try to detect possible differences in structure caused by the phenomenon of adsorption. However, in the range of magnifications offered by this type of microscope, often visible and concrete change is not obvious, so sometimes the solution is to use significantly higher magnification provided by TEM (Transmission Electron Microscope). The only thing that can be noticed is that adsorption slightly reduces the number of open pores on the surface, which is probably caused by their filling by the substance being adsorbed.



a)



b)



c)

Fig 3. 1000x magnification SEM images of bentonite after adsorption, for different initial concentration of Pb^{2+} ions a) 200mg/L b) 300mg/L c) 400mg/L

3.1.3. XRF analysis

Chemical composition (in the form of oxides) of bentonite was determined by XRF analysis and the results were presented in Table 1. As can be seen, the sample consists mainly of SiO₂ (54.74%), and Al₂O₃ (28.07%), indicating that it is an aluminosilicate material. High levels of Al₂O₃ indicate the presence of aluminum oxides or substitution of Si by Al [13]. Oxides, as Fe₂O₃ (6.95%), Na₂O (4.03%), MgO (2.35%) and CaO (2.29) are detected in lower concentrations, while other oxides are present in the percentage lower than 1. The presence of MgO, Na₂O, CaO, and K₂O indicate that these are the main exchangeable cations in bentonite [13].

3.1.4. DTG analysis

In order to test the thermochemical changes, TG/DTG analysis of bentonite was performed, and the appropriate profile is shown on Fig. 4. The sample of bentonite is characterized by a three-step weight loss profile during heating in the flow of N₂ up to 1000°C. The first step (from room temperature to 99°C) corresponds to the weight loss of 11.2% and can be ascribed to the loss of absorbed water. With further heating up to 182°C, the mass of the sample reduces by additional 2.5%, which is due to the loss of interlayer water. In the third step (in the temperature range 182°C - 561°C), the weight of the sample decreases for extra 5.9%, as a consequence of dehydroxylation minerals (DTA).

Table 1. Chemical composition of bentonite obtained by XRF

Chemical composition	SiO ₂	Al ₂ O ₃	CaO	K ₂ O	Fe ₂ O ₃	ZnO	Na ₂ O	MgO	TiO ₂	SO ₃	P ₂ O ₅	SrO	ZrO ₂	Sum
wt%	54.74	28.07	2.29	0.37	6.95	0.02	4.03	2.35	0.79	0.07	0.06	0.03	0.05	99.82

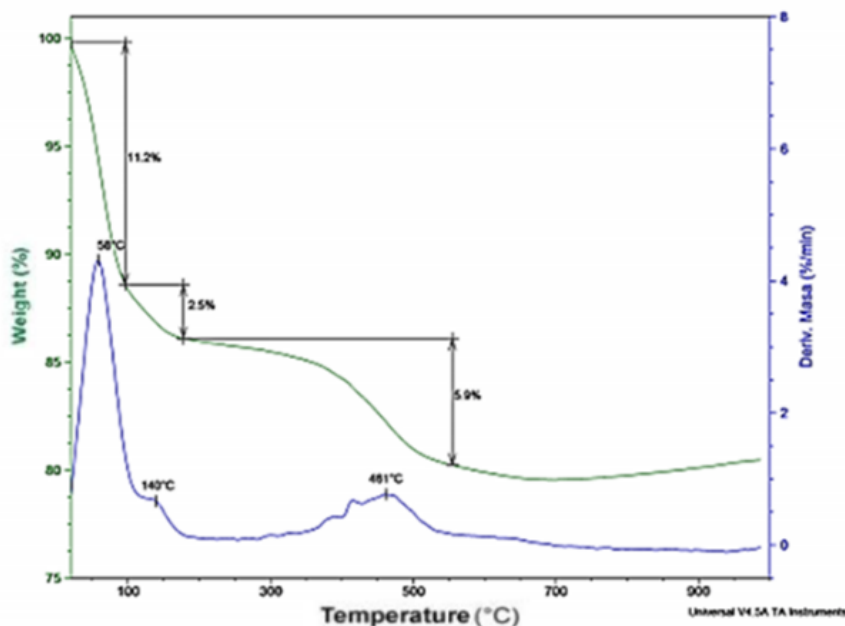


Fig. 4. TG/DTG profile of bentonite

3.2. Adsorption experiment

Batch experiments were carried out to evaluate the effect of initial lead (II) concentration (200, 300 and 400 mg/l) on its removal efficiency by using bentonite, and to evaluate the quality of fitting the Freundlich and Langmuir adsorption isotherm to the experimental data. Experiment conditions are: bentonite dosage 1 gram, 50 ml of lead (II) solution, contact time 2.5 minutes, stirring rate 100 rpm, temperature 25°C, pH value 5.

3.1.4. Removal efficiency

Figure 5. shows the effect of the initial lead (II) concentration on removal efficiency, which is calculated

by using equation (1). Removal efficiency is high for all three examined initial lead (II) concentrations, and it is above 99%. However, Fig.5. shows that the lead (II) removal efficiency slightly decreases with an increase in initial lead (II) concentration. An increase in initial lead (II) concentration reduces adsorption sites, since more ions are introduced into the system, therefore, with time the system will approach a saturation phase. At lower concentration, more adsorption sites are available and adsorption is high, but as the concentration increases, the adsorption sites become the limiting factor hence resulting in lower adsorption [13].

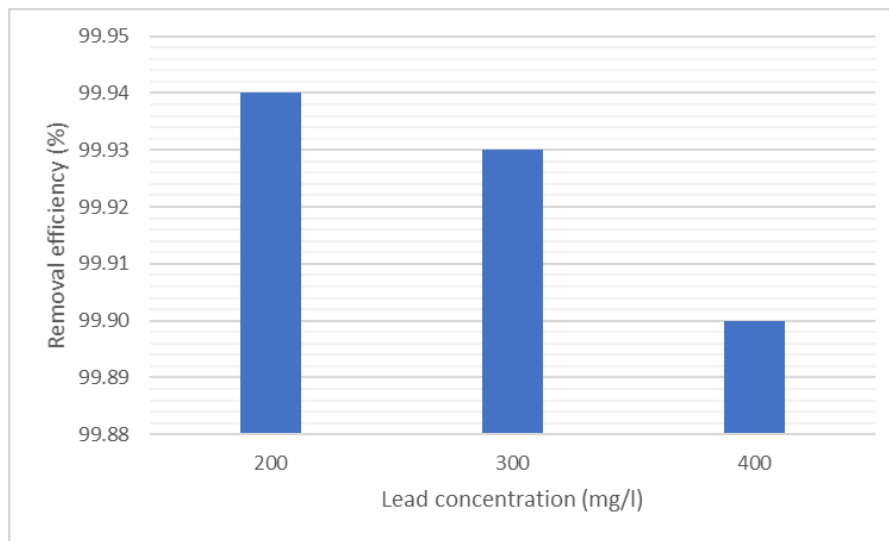


Fig.5. The effect of the initial lead ions concentration on removal efficiency

3.2.2. Adsorption isotherms

The quality of the isotherm fit to the experimental data is typically evaluated based on the magnitude of the correlation coefficient for the regression; i.e. the isotherm giving an R^2 value closest to unity is considered to give the best fit [17].

The amount of lead (II) adsorbed per unit weight of adsorbent, q_e , is calculated by using equation (3), and then based on the equation (2), Freundlich constants K_F and n can be determined from the plot of $\log q_e$ versus $\log C_e$ (Figure 6). The plot of $\log q_e$ versus $\log C_e$ has a slope with the value of $1/n$ and an intercept magnitude of $\log K_F$.

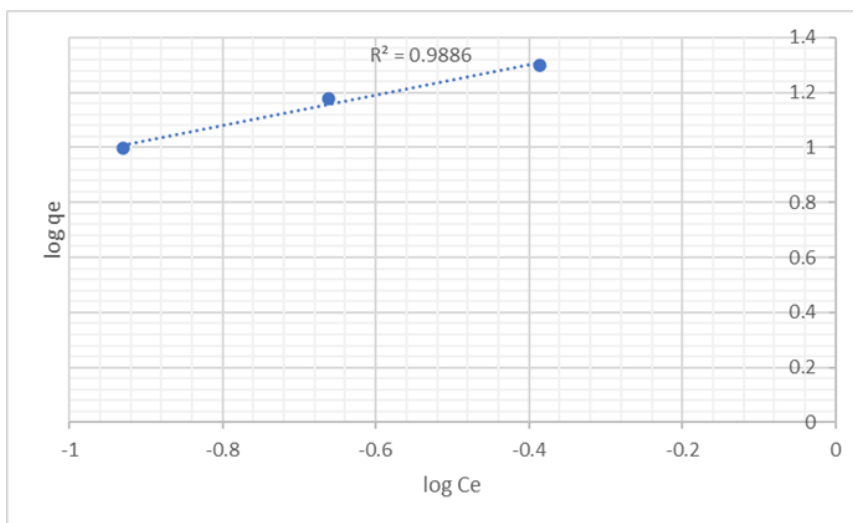


Fig.6. Freundlich adsorption model for adsorption of lead (II) on bentonite.

The Langmuir equation (4) can also be written in the following form:

$$\frac{1}{q_e} = \frac{1}{q_{max}} + \frac{1}{K_L q_{max} C_e} \quad (6)$$

Langmuir constants K_L and q_{max} can be determined from the plot of $1/q_e$ versus $1/C_e$ (Figure 7). The plot of $1/q_e$ versus $1/C_e$ has a slope with the value of $1/K_L q_{max}$ and an intercept magnitude of $1/q_{max}$.

Determined values of all the parameters from Freundlich and Langmuir equations are summarized in

Table 2. The adsorption isotherm data are better fitted with the linearized Langmuir equation isotherm, giving an R^2 value closest to unity (0.9994), than with linearized Freundlich equation (0.9886). These results are consistent with some previous studies of adsorption isotherms for lead adsorption, using bentonite from different deposits [9, 17].

Maximum adsorption capacity (q_{max}) of bentonite for lead (II), determined from Langmuir equation, is 33.8359 mg/g.

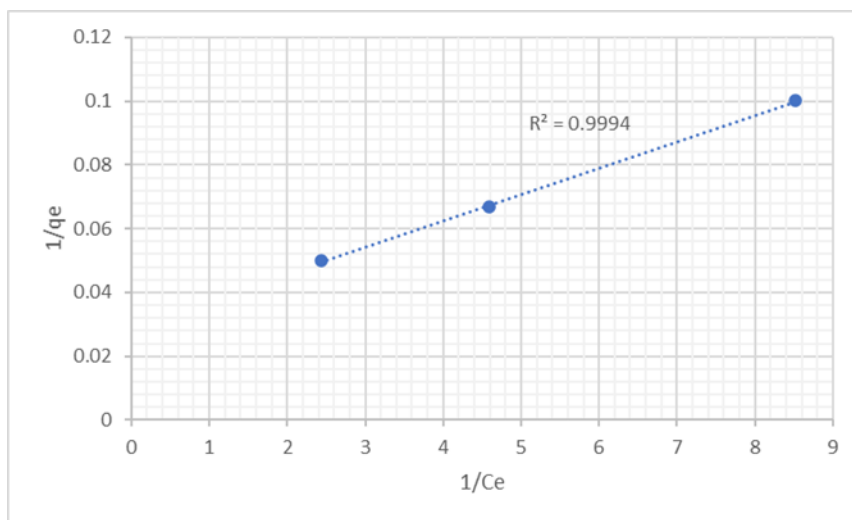


Fig.7. Langmuir adsorption model for adsorption of lead (II) on bentonite.

Table 2. The Freundlich and Langmuir equation parameters determined from adsorption isotherms

Isotherm parameters	Value
Freundlich	
K_F (mg/g)	33.2917
N	1.8131
R^2	0.9886
Langmuir	
q_{max} (mg/g)	33.8359
K_L (l/mg)	3.5836
R^2	0.9994

IV. CONCLUSION

Biosorption performance of natural bentonite from deposit Šipovo in Bosnia and Herzegovina was investigated, for the removal of lead (II) from aqueous solutions. The adsorption of lead (II) on bentonite was very fast, and it is achieved a removal efficiency over 99% for a short contact time of 2.5 minutes, at temperature of 25°C, and with bentonite dosage of 1g. The results showed that increasing the initial lead (II) concentration decreased removal efficiency due to the saturation of bentonite with lead (II). Experimental results are in good agreement with Freundlich and Langmuir isotherm models. Obtained value of constant n (1.8131) from Freundlich adsorption isotherm showed that adsorption is favorable. However, it was found that Langmuir adsorption model is fitted better with obtained experimental data, with regression coefficient of 0.9994. Maximum adsorption capacity obtained from Langmuir adsorption model is 33.8359 mg/g.

The results of this research demonstrated that natural bentonite can be considered as a promising adsorbent material for the development of a low cost biosorption technology for the removal of lead (II) from aqueous solutions, such as wastewaters.

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