Physical and Chemical Characterization of Agricultural Waste and Testing of Sorbtion Abilities for Removal of Heavy Metals from Aqueous Solutions

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ABSTRACT

The problem of environmental pollution is more expressed and more present by the development of the industry and the growth of the human population. Pollution of natural and wastewater is most often due to the release of heavy metals into watercourses. The greatest challenge for researchers is choosing the right biomass from a large number of low-cost biomaterials, and availability and price are very important selection factors. Microbial biomass, forestry waste and agroindustrial complexes are most frequently examined, as well as various macromolecules of natural origin. In this paper, barley straw that arises as agricultural waste product in barley production in Bosnia and Herzegovina, was used as a biosorbent. In the experimental part, physical and chemical characterization of barley straw was performed, after which the efficiency of removing Cd(II) and Ni(II) from aqueous solutions, using barley straw, and the influence of process parameters (pH value of aqueous solution, biosorbent size, interaction of metal ions) on the biosorption capacity were tested. It can be concluded that barley straw has good adsoption characteristics for the use as a low-cost natural sorbent for the removal of heavy metals from water.

Keywords-- Cadmium, Nickel, Physical and chemical characterization, Sorption.

I. INTRODUCTION

Heavy metals can be found in natural aquatic systems in the form of free ions, complexes with organic and inorganic ligands, dispersed colloids, etc. In which forms heavy metals will be found in nature depends primarily on the pH of natural water, the oxidizing and reduction metal properties and the aquatic environment, the type and concentration of available ligands [1].

The concentration of cadmium in aquatic systems depends on the environment conditions, since it can exist in the form of a free ion, ion bound to a complex with dissolved organic matter, and reciprocally or irreversibly adsorbed on suspended particles and sediment [2]. Nickel is found in various valence states in the environment, with +2 being the most common. It forms stable chelating cationic and anionic structures.

Sorption in the broadest sense implies a change in the concentration of some of the components at the boundary surface of the heterogeneous system phase [3]. The attractive forces of molecules, atoms or ions on the surface of the solid phase are not balanced, which makes the particles on the surface of the solid phase, when they come into contact with the gas or liquid phase, tend to bind molecules or ions from that second phase. The nature of inter-group interactions determines the existence of an energy field at its solid phase, therefore the surface prefers the attraction and binding of certain components, and the sorption is limited by the size of

the contact surface, the number and dimensions of the pores [4].

In order to examine the various effects of the adsorption of some sorbates on a particular sorbent and determine the nature of this sorption, laboratory tests are carried out, usually in batch conditions, and various mathematical models are used to process the obtained experimental data [5]. The amount of adsorbed matter per adsorbent mass unit (q) is calculated using the equation:

$$q = \frac{(C_o - C) \cdot V}{m}$$

where-
C_o is the initial concentration of the sorbate,
C is the concentration of the sorbate in equilibrium,
m is the mass of the sorbent,
V is the volume of the solution.
On the basis of the obtained experimental data, the sorption efficiency can also be calculated using the equation:

$$\text{Efficiency}(\%) = \frac{C_o - C}{C_o} \cdot 100$$

The unique and diverse chemical structure of biological materials, which is reflected in the presence of various functional groups on surfaces that have high affinity for binding of heavy metals, makes these materials suitable and attractive as sorbents for the removal of heavy metals. Metals can bind to biomass by adsorption processes, pore complexing, ion exchange, and hemisorption [6]. For the industrial application of biosorption it is very important to determine the efficiency of the given adsorbent for the target pollutant. Binding heavy metals can involve multiple mechanisms influenced by various physical and chemical factors, and they determine the effectiveness of adopting for a given biosorbent. Therefore, the individual and overall effects of various factors on biosorption must always be determined.

In recent decades, more attention of researchers is focused on waste plant materials as low-cost and widely available biosorbents for removing heavy metals from water. A number of papers have reported on the possibilities of using agricultural wastes, such as: maize leaf [7-10], rice husk [11-14], nut shells [15-18], straw [19-22]. Some of the advantages of using plant wastes for wastewater treatment include simple technique, requires little processing, good adsorption capacity, selective adsorption of heavy metal ions, low cost, free availability and easy regeneration [23].

Bosnia and Herzegovina has significant quantities of barley (*Hordeum vulgare* L.) straw, that emerges as waste product in primary agricultural production. The possibility of using barley straw as biosorbent for removal of heavy metals from aqueous solutions would provide an alternative to conventional purification methods, where barley straw as the new low-cost adsorbent could represent the principle of sustainable development and environmental conservation.

The aims of the experimental work were as follows:
1) To perform physical and chemical characterization of barley straw,
2) To examine the efficiency of removing Cd(II) and Ni(II) from aqueous solutions using barley straw as biosorbent, and
3) To determine the influence of process parameters (pH value of aqueous solution, biosorbent size, interaction of metal ions) on the biosorption capacity.

The material used in experimental work was barley staw, which is collected after the harvest of barley.

II. METHODOLOGY

The content of moisture and ash in material was determined by gravimetric method.

Alkaline and alkaline earth metals (K, Na, Ca and Mg) were determined by spectrophotometric methods, in aqueous solution after the straw was rinsed with distilled water, and in rinsed barley straw.

Volumetric method with $KMnO_4$ was used to determine organic matter in barley straw. In order to examine the charge of the surface of the biosorbent itself, the points of zero charge were determined.

The cation exchange capacity (CEC) of barley straw was determined by the standard method of ion exchange procedure with NH_4Cl. The morphology of the barley straw sample, before and after adsorption of metal ions, was examined by the scanning electronic microscope VEGA 3 SEM TESCAN at an acceleration voltage of 20 kV, at various increments, and FTIR method was used for qualitative analysis of functional groups.

The sorption capacity of the biosorbent was tested in the pH range of 2 to 6, using 0.5 mm and 0.8 mm sorbent granulation, at constant temperature of 25°C and mixing speed of 300 rotations per minute (rpm). Experiments were conducted first for single systems of metal ions, and then for a mixture of metal ions, i.e. binary solutions. The pH values were adjusted with a solution of HNO_3 or NaOH with concentration of 0.1/0.01 M. Potentiometric method was used to adjust and measure the pH value using a pH-meter with a combined electrode of Metller Toledo MP 220. The initial concentrations of Cd(II) and Ni(II), in their single and binary systems were 10.0 mg/L for each metal ion. The samples for the analysis of the metal content were taken over a period of 100 min, at time intervals of 5, 10, 20, 30, 50 and 100 min. After each sample was taken, the pH was measured on the pH meter and the contents of cadmium and nickel, which remained in the their individual water solutions after the adsorption process, were determined, as well as cadmium and nickel content from the binary solutions.

To determine the concentration of cadmium and nickel in synthetic aqueous solutions before and after sorption, a spectrophotometric method was used using an optical emission spectrophotometer Perkin Elmer ICP OPTIMA 2100 DV.

III. RESULTS AND DISCUSSION

3.1. The results of physical and chemical characterization

The moisture content in the biosorbent was 7.064%, which can be considered relatively small. The biosorbent does not retain a large amount of water in its structure, which is why it can be stored in the air without glutinating the particles and changing the granulation. This feature is of special importance for easy handling of biosorbent in applications in large water purification systems. The ash content was 4.06%. The ash content comes from mineral substances (alkaline and alkaline earth metals) which the plant accumulates during its growth.

An analysis of the alkaline and alkaline earth metals in the solution, after the straw was rinsed with distilled water, was made to show the leaching of these metals, as well as to determine which amount of these metals passed into the solution, which remained in the straw, and which will later on during adsorption to participate in the ion exchange. After calculating the degree of excretion, the concentration of alkaline and alkaline earth metals that has passed into the solution and the concentration of K, Na, Ca and Mg metals remaining in the straw, which will participate in the exchange with Cd(II) and Ni(II) ions by the sorption process from aqueous solutions, were determined (Table 1).

Table (1): The content of alkaline and alkaline earth metals in straw and solution after the straw was rinsed with distilled water.

Ion	Na^+	K^+	Mg^{2+}	Ca^{2+}
The excreted ion quantity after the rinsing using distilled H_2O (mmol/g)	0.002	0.056	0.0075	0.014
The metal quantity in barley straw after rinsing (mmol/g)	0.078	0.368	0.054	0.095
Excretion degree (%)	2.56	15.2	13.88	14.73

Based on the degree of excretion, it can be seen that the ions are excreted in the following order:

$$K^+ > Ca^{2+} > Mg^{2+} > Na^+$$
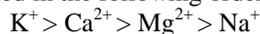
The content of total organic matter in barley straw water was determined on the basis of the $KMnO_4$ consumption, where the content of the oxygen required for the oxidation of organic matter in water was calculated. Consumption of oxygen was 1.34 mg/l.

The obtained test results of the biosorbent surface charge are shown in Figure 1.
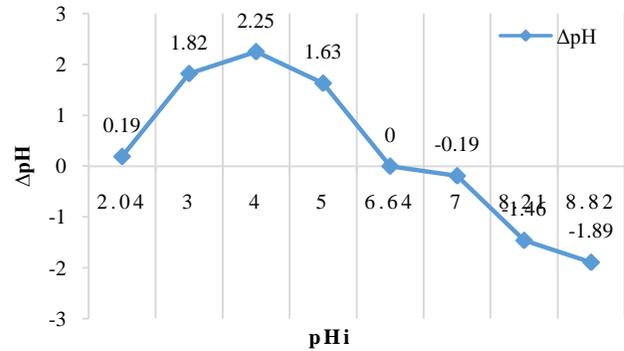
Figure 1: The changes in pH during the determination of the pH of zero charge

The pH value of the zero charge potential of barley straw biosorbent is 6.61. This implies that under the pH value of 6.61 of the solution, the biosorbent will be positively 3.charged, while above this value, its charge will be negative. The experimental results have shown that the maximum adsorption capacity is at pH values between 5 and 6, i.e. near the zero charge point. At lower initial pH values (pH<5.0) where the barley straw surface is positively charged, lower absorption capacities are observed due to the action of the reflective forces.

Although this value is relatively high, it exhibits significant sorption activity towards metal cations at lower pH values as well, where its total positive charge is expected. It is assumed that the reason for this phenomenon is a significant share of the ionic exchange in the metal ion sorption mechanism, whereby the deprotonation of functional groups is carried out at pH below the point of zero charge (pzc).

The cation exchange capacity (CEC) of barley straw is the ability of sorbents to adsorb cations from aqueous solutions. It is expressed as the number of mmol/g. CEC in barley straw was determined by the standard method of ionic exchange with NH_4Cl. The amount of alkaline and alkaline earth metal ions which have passed into the solution after addition of NH_4Cl is shown in Figure 2. The total exchange of all cations was 2.16 mmol Me^{z+}/g (Me^{z+} - metal ions). On the basis of the obtained results, it can be seen that Ca ion is dominant in relation to other metals, which means that Ca ions of barley straw will probably be replaced by Cd or Ni ions, by the principle of ion exchange, and that ion exchange plays a major role in the binding process of the examined ions.
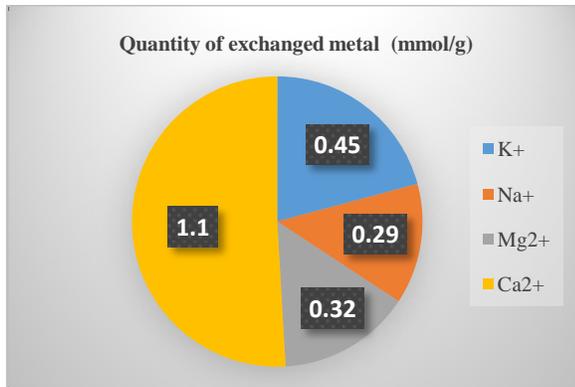
Figure 2: The content of exchangeable cations of alkaline and alkaline earth metals in straw

The total exchange of all cations was 2.16 mmol Me^{z+}/g (Me^{z+} - metal ions). On the basis of the obtained results, it can be seen that Ca ion is dominant in relation to other metals, which means that Ca ions of barley straw will probably be replaced by Cd or Ni ions, by the principle of ion exchange, and that ion exchange plays a major role in the binding process of the examined ions.

SEM micrography was made for native and active biosorbent where visual morphology was observed, with significant differences in barley straw structure before and after the adsorption process of Cd(II) and Ni(II) ions. In Figures 3. to 5. the morphology of barley straw was shown before and after activation with Cd(II) and Ni(II) ions. After Cd and Ni ions adsorption on barley straw, there is an altered morphology in relation to barley straw prior to the adsorption process. These changes in the structure indicate that metal sorption is associated with chemical changes on the surface of biosorbent. SEM micrographs also show that the morphological changes in the surface of the biosorbents after Cd and Ni ions sorption depend on the nature of the adsorbed material, that is, the ionic radius, which is why the surface changes of the sorbents after the sorption process are different for Cd and Ni ions.
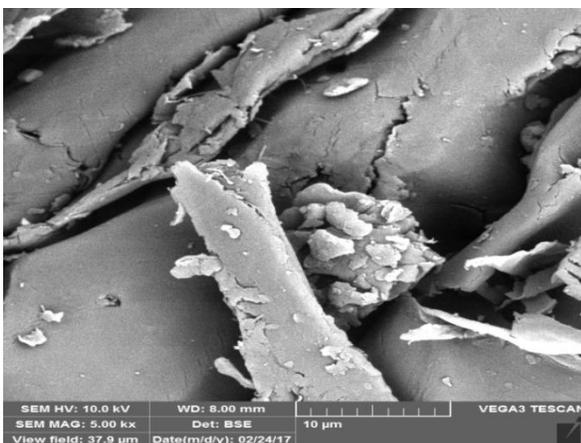
Figure 3: SEM of untreated barley straw
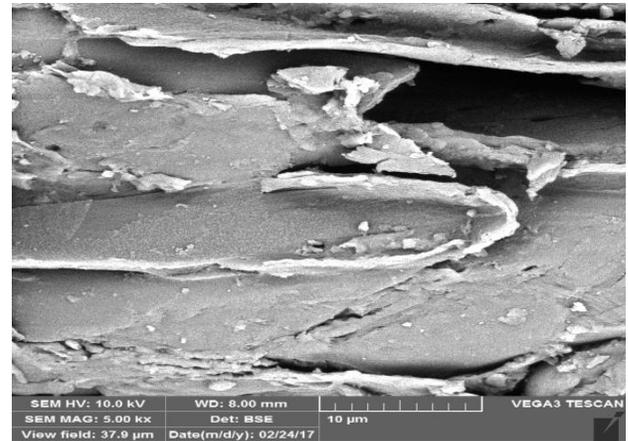
Figure 4: SEM micrography of barley straw after adsorption with Cd ions (magnified 5000x)
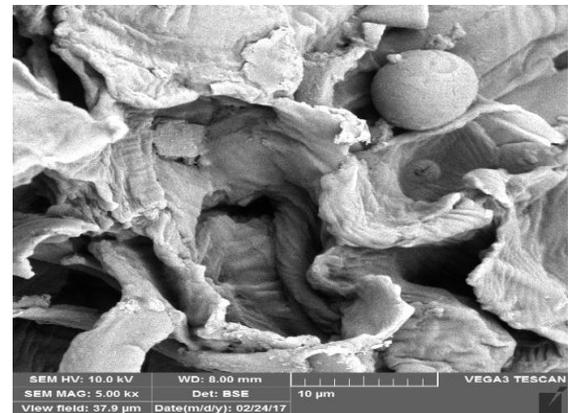
Figure 5: SEM micrography of barley straw after adsorption with Ni ions (magnified 5000x)

The assumption that there is an exchange in metal ions with hydrogen ions and ions of alkaline and alkaline earth metals has been confirmed by the FTIR analysis of barley straw of native adsorbent as well as after adsorption with Cd and Ni ions. In Figures 6. to 8. FTIR spectra for barley straw biosorbent spectra are presented before and after adsorption with Cd and Ni ions.

Figure 7: Native biosorbent
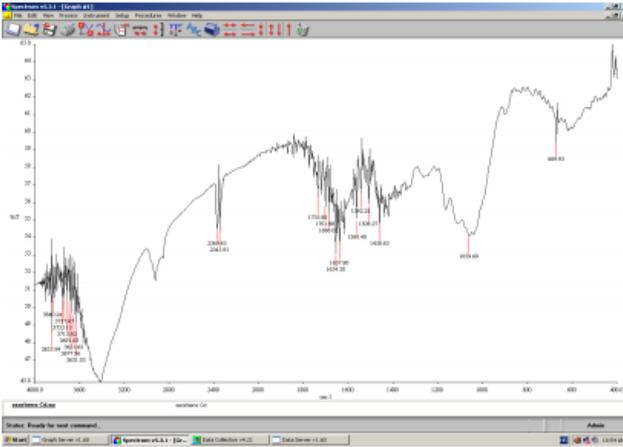
Figure 8: Biosorbent after adsorption with Cd ions

Figure 8: Biosorbent after adsorption with Cd ions

Peaks existing in the FTIR spectrum of the biosorbent based on barley straw belong to numerous functional groups and chemical bonds.

The peak at 3400 cm^{-1} (which usually appears in the range of 3200-3600 cm^{-1}) belongs to the valence band of the O-H group. The peaks in the interval of 1654-1618 cm^{-1} can be attributed to the C=O group, but to some extent they overlap with the valence bands of the C=C bond of the aromatic ring that exists in the lignin composition. Also, N-H valence vibrations have similar wave numbers. The peak at 2925 cm^{-1} indicates symmetric or asymmetric -C-H valency vibration of aliphatic acids. It can also be associated with the existence of a -C-O-vibration from alcohol or carboxylic acids that are presumed to represent key binding spots for heavy metals.

The obtained results of the removal efficiency of Cd and Ni ions in their individual systems are shown in Figures 6. to 9. From the results shown, it can be noticed that as the pH values of the sorbate increases, the sorption capacity increases according to the investigated metal ions. At the initial pH value of 2.0, the biosorption capacity is fairly small, which means that in these conditions only 4.77% Cd and 12.03% Ni were removed on the biosorbent granulation

of 0.5 mm. One of the reasons is the protonation of functional groups on the surface of adsorbents of hydrogen ions from the solution. Minimal sorption at high acidity of solution could be explained by high concentration and high mobility of H^{+} ions, so hydrogen ions are primarily adsorbed at sorption positions compared to metal cadmium and nickel ions, which indicates that the process, in addition, features ion exchange [24].

As the pH of the solution increases, the biosorption capacity increases for both types of heavy metals ions and at a pH values between 5.0 and 6.0 reaches its maximum. The maximum sorption of the tested metals was reached at pH 5 when 92% of nickel and 86.7% of cadmium were removed. The reason is that on the biosorbent surface, as the pH values increase, deprotonation of the functional groups occurs and results in the surface becoming less positively charged and thus having a higher affinity for the cations from the solution.
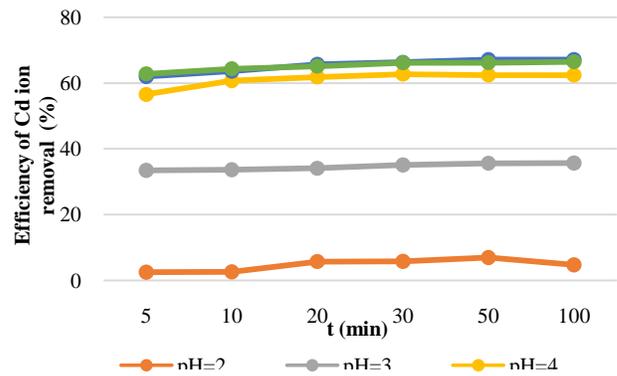
Figure 6: Efficiency of Cd^{2+} removal at different pH values and biosorbent granulation of 0.5 mm
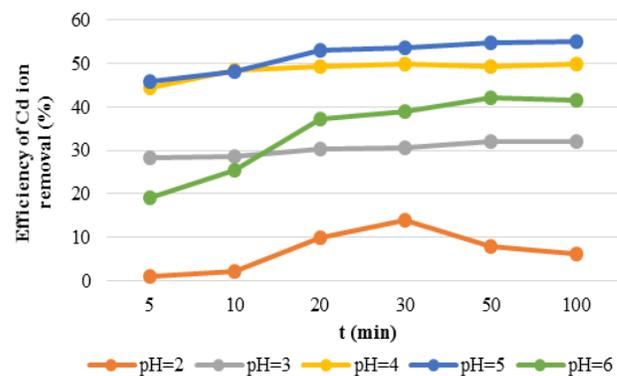
Figure 7: Efficiency of Cd(II) removal at different pH values and biosorbent granulation of 0.8 mm
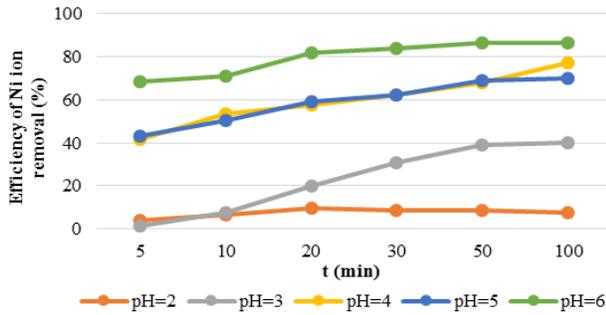
Figure 8: Efficiency of Ni(II) removal at different pH values and biosorbent granulation of 0.5 mm
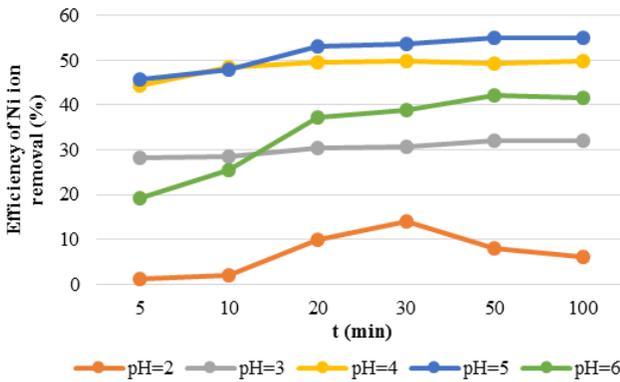
Figure 9: Efficiency of Ni(II) removal at different pH values and biosorbent granulation of 0.8 mm

In order to determine the efficiency of the biosorbent in more complex systems similar to real effluents, tests of the biosorption process in binary systems were conducted, i.e. in solutions containing both cadmium and nickel ions, usingt different granulations. Comparison of individual and mutual effect of Ni i Cd ions on the process of biosorption on sorbent of different granulation is shown in Figure 10.
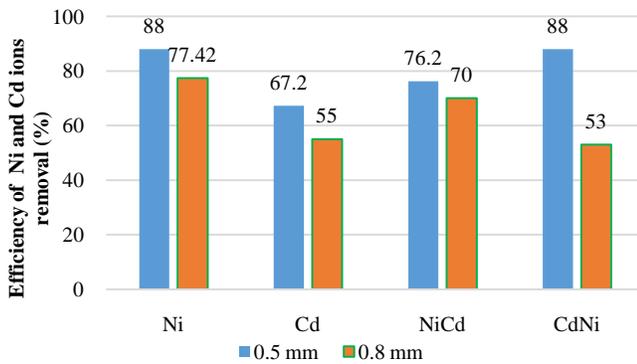
Figure 3.10: Individual and mutual effect of Cd(II) and Ni(II) ions on the biosorption process

It has been observed that the efficiency of removing heavy metals ions from the solutions containing the individual ions, ie. from single systems is increased in relation to the efficiency of removal of the metal ions when they are found as a binary solution. The results of the study showed that more Ni(II) ions were removed from the binary Cd(II) and Ni(II) mixture in relation to Cd(II) ions, and that the removal efficiency rate increases with particles decreasing, and by increasing the pH value. The higher removal efficiency of the Ni (II) ions removal is due to the degree of electronegativity and ionic radius compared to Cd(II) ions. Also, the larger contact surface of biosorbents using a 0.5 mm granulation gave better removal efficiency of both metal ions. Higher ions hydration favor the removal from the adsorbent surface and the sorption is weaker. Since the attraction of the water molecule around the ions depends on the ion charge density, the smaller ions will attract more water molecules leading to the inverse relationship between the ionic radius and the hydrated ionic radius. Also, the greater the electronegativity, the stronger is the bond that is established between metal ions and oxygen atoms from functional groups on the surface of biosorbent, where electronegativity is based on the Pauling scale of electronegativity for Ni(II) 1.8 and for Cd(II) 1.7.

IV.   CONCLUSION

The content of moisture and ash in the biosorbent is very small, indicating that the biosorbent does not retain a large amount of water in its structure and can be stored in the air without glutinating the particles and changing the granulation, which is very important in the treatment of wastewater. The small ash content is mainly due to alkaline and alkaline earth metals. SEM analysis of untreated barley straw has showed irregular morphology of the surface, in the presence of numerous micro and macro pores that are a prerequisite for high ability of sorption of heavy metals. After the adsorption of Cd(II) and Ni(II) ions on the barley straw, the changed morphology in relation to barley straw occurs before the adsorption process. These changes in the structure indicate that metal sorption is associated with chemical changes on the biosorbent surface of, which is further confirmed by the FTIR analysis. Using the FTIR analysis of barley straw of native adsorbent as well as adsorbents after adsorption with Cd(II) and Ni(II) ions, confirmed the assumption that there is an exchange in the metal ion with hydrogen ions and ions of alkaline and alkaline earth metals. Comparison of the FTIR spectrum after adsorption of the Cd(II) and Ni(II) ions indicates that the wavelength values move in a region dominated by strong C-O, C=O and C=C. These functional groups are highly reactive and are deprotonated during the adsorption process. Changing the pH value during straw rinsing with distilled water is the result of the excretion of alkaline and alkaline earth metals from the biosorbent surface. The excretion of ions is carried out in the following order: $K^+ > Ca^{2+} > Mg^{2+} >$

Na^+. This shows that initially the K^+ and Ca^{2+} ions from barley straw will be replaced with Cd^{2+} or Ni^{2+} ions by the ion exchange principle, and that ion exchange plays a major role in the binding process of the investigated ions. Based on the obtained value of the cation exchange complex, it can be concluded that Ca^{2+} ion from biosorbent is dominant during the ion exchange mechanism with Cd(II) and Ni(II) ions. Sorption of Cd(II) and NI(II) ions is the most effective in the range of pH between 5 and 6, at an adsorbent dose of 1 g. At pH 5, the best effect of sorption is obtained, when 92% of Ni and 86.7% of Cd are removed in the biosorbent granulation of 0.5 mm. At lower pH values, the effect of sorption is very small, which is attributed to the protonation of functional groups on the adsorbent surface with hydrogen ions from the solution, while at pH values above 6, the metal is released into the form of hydroxide and the precipitation occurs, so the reduction of the ion concentration in the solution cannot be attributed to the adsorption phenomena. The affinity of barley straw towards Cd(II) and Ni(II) ions correlates with the physical and chemical properties of a given metal ion. A smaller ionic radius, and a higher degree of electronegativity of Ni(II) ion compared to Cd(II) ions is the result of higher removal efficiency of Ni(II) ion. Comparing the adsorption capacity of individual Cd and Ni ions, and the sorption capacity in their binary solutions, it can be concluded that there is a slight reduction in the removal of these ions from binary solutions in relation to individual solutions, which means that to a lesser extent adsorption of one ion is suppressed by adsorption of the other.

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