Removal of Cd and Ni Ions from Water Using Biosorbent Based on Corn Residues

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ABSTRACT
Water sources have become unsafe for human consumption, but also for use in agriculture for irrigation or for the food industry. The deteriorating water quality has led to a shortage of drinking water supply. The aim of this study was to examine the possibility of using agricultural waste, specifically corn residues, (corn cob and silk) as a bioadsorbent to remove Ni and Cd ions from water. Experimental results have shown that corn residues (corn cob and corn silk) have a certain potential for use as bioadsorbents. The possibility of application was tested for corn cob and corn silk (corn cob 3.5g and corn silk 1.5g) for metal concentrations of 20, 40, 100 mg/L for corn cob, and 40 mg/L and 100 mg/L for corn silk. The tests were performed at pH 3 and 6 at a contact time to reach equilibrium of 3.5 hours. Adsorption parameters were determined using the Freundlich isotherm. The morphology of biosorbents before and after the adsorption process was monitored to observe differences in the structure of the biosorbents used.

The results showed that in the case of Cd\(^{2+}\) ions, with an initial concentration of 100 mg/L, the highest removal efficiency was achieved for all samples used, while in the case of Ni\(^{2+}\) ions the highest removal efficiency was achieved at an initial concentration of 40 mg/L for all samples, while the corn silk based of the maize (Zea mays L.) sample proved to be the best for the removal of these ions where the influence of pH has a great influence on the removal efficiency as well as the physico-chemical properties of the metal. Morphological analysis of samples before and after the adsorption process showed significant differences in the structure of the biosorbents used, which lead to the conclusion that sorption is associated with chemical changes on the surface of the biosorbent.

The calculated values of the parameters used in the Freundlich isotherm indicated the existence of high-energy sorption centers in the biosorbent of corn cob and corn silk hybrids maize, and that the adsorption was more pronounced at lower pH values. The corn cob-based of the maize (Zea mays L.) biosorbent used has been shown to be a heterogeneous surface biosorbent with moderate sorption intensity to Ni and Cd ions in corn silk-based biosorbent.

Keywords- corn cob, corn silk, maize (Zea mays L.), hybrid maize, biosorption, nickel, cadmium.

I. INTRODUCTION
Wastewater can be of different origins, depending on its chemical composition. [1] In order to achieve efficient and economically acceptable removal of toxic substances, it is very important to perform wastewater characterization. Characterization is performed according to physical properties, chemical properties and biological characteristics in order to be able to select the appropriate wastewater treatment. The composition of wastewater depends on the raw material, technological processes and waste products. [2]

Chemical compounds in wastewater have a potentially negative effect on the biological system, and at the same time make successful biological treatment difficult. The Figure 1. shows the groups of impurities present in natural waters.

Figure 1: The groups of impurities present in natural waters

All the pollutants in water, heavy metal ions are most often present, which, in addition to being very toxic, biologically and thermally non-degradable, also have the
property of accumulation in the tissues of organisms. 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. [3]

Heavy toxic metals such as Pb, Cu, Zn, Cd, Ni enter water bodies through wastewater from the metal industry and the Cd-Ni battery industry, phosphate fertilizer, mining, pigment industry, stabilizers, galvanic alloy industry, etc. Since these heavy metals are captured in the food chain and due to their tendencies as bioaccumulation it is necessary to remove them from wastewater.

Among the numerous methods used today for the purification of aqueous systems from heavy metals, adsorption can be singled out due to the high efficiency, economy and availability of natural and synthetic adsorbents. [4] Therefore, due to this fact, natural adsorbents, i.e. biosorbents generated from industrial processes, are increasingly used, as well as agricultural waste. [5] It is generally known that large areas of arable land in Bosnia and Herzegovina are under maize. After harvesting, the same large amounts of corn residues remain on the soil surface or are plowed. Therefore, in this paper, two types of maize were used as a biosorbent: maize (Zea mays L.) and hybrid maize, using corn silk and corn cob of both biosorbents to select a material with better adsorption properties to remove Ni and Cd ions from aqueous solutions. As the adsorption process itself is affected by the pH value, type and concentration as well as the nature of the adsorbent itself, these parameters were examined, as well as the calculated values of the Freundlich constants from the Freundlich adsorption isotherm.

II. EXPERIMENTAL PART

2.1 Material

In this work, samples of hybrid corn cob and corn silk, and maize (Zea mays L.) corn cob and corn silk were used, which were washed with distilled water and air - dried, then ground into powder and divided into fractions according to particle size using mesh grids of different sizes. Particles with a granulation of 1 mm were used in the paper. The biosorption capacity of heavy metal ions Cd$^{2+}$ and Ni$^{2+}$, using corn cob and silk was tested in a model aqueous solution of ions of given heavy metals.

2.2. Methods

In dose gasks prepared 100 ml of solutions of Ni(NO$_3$)$_2$ and CdCl$_2$ as substrates of heavy metals of the following concentrations: 100 mg/L, 40 mg/L, 20 mg/L for sample based on corn cob and 100 mg/L; 40 mg/L for sample based on corn silk.

The mass of the biosorbent was 3.5 g, for samples based on corn cob and 1.5 g for samples based on corn silk, ie 0.035 mg/L and 0.015 mg /L. The influence of pH (3 and 6) was monitored using a pH meter type Mettler Toledo MP220, on the amount of adsorbed ions. The contact/mixing time at 250 rpm was 3.5 hours. The pH value was adjusted by adding 0.01 mol L$^{-1}$ HNO$_3$ and 0.01 mol L$^{-1}$ NaOH.

After completion of the adsorption, the solution was filtered and the concentration of residual heavy metal ions was determined after the completion of the biosorption process on an Perkin Elmer atomic absorption spectrophotometer.

The mixer - Rotamix SHP-10 Scale was used in the work, to perform the process of biosorption of Cd$^{2+}$ and Ni$^{2+}$ ions from the prepared model solutions. For precise weighing, an analytical balance was used - Mettler Toledo AB 104-S, with an accuracy of 4 decimal places.

The biosorbent sample before and after the biosorption process was examined with an optical microscope (Olympus BX50) equipped with a microphoto camera (Olympus DP 10 camera).

Biosorption capacity and removal rate were calculated using the equations, respectively:

$$q_e = \frac{S_o - S_e}{X}$$

$$\% = \frac{S_o - S_e}{S_o} \times 100$$

where is:

- $q_e$ - adsorbent biosorption capacity;
- $S_o$ - concentration metal ion before adsorption;
- $S_e$ - concentration metal ion after adsorption;
- $X$ - mass biosorbent (g/l).

The values of the Freundlich constants from the Freundlich adsorption isotherm were calculated [6]:

$$\log q_e = \log K_f + \frac{1}{n} \log S_e$$

where is:

- $q_e$ - amount of adsorbate adsorbed per unit weight of adsorbent (mg / g);
- $K_f$ - temperature-related parameter;
- $n$ - characteristic constant for the investigated adsorption system and are read from the diagram ($\log q_e$) = $f$ ($\log C_e$).

III. RESULTS AND DISCUSSION

From the results shown in Figure 2. for the hybrid corn sample, it can be seen that the highest percentage of removal was from a solution of initial concentration of 100 mg/L Cd$^{2+}$ ions at pH 3 32.4%, while the highest % of removal for Ni$^{2+}$ ions was from the initial concentrations 40 mg/L Ni$^{2+}$ at pH 6 when it was 30%, while other solutions when it came to Ni$^{2+}$ showed a very low % removal.
Figure 2: Efficiency of Cd(II) and Ni (II) removal at pH values 3 and 6; initial concentrations 20 mg/L, 40 mg/L, 100 mg/L using hybrid corn cob as biosorbent

Based on the results shown in Figure 3, for the sample of biosorbent based on corn silk hybrids, it can be seen that the highest % removal for Cd$^{2+}$ ions 34.4 % was recorded from a solution of initial ion concentration 100 mg/L at pH 3, and for Ni$^{2+}$ ions at initial at a concentration of 40 mg/L at pH 3 where the % removal was 35.5%.

Figure 3: Efficiency of Cd(II) and Ni (II) removal at pH values 3 and 6; initial concentrations 40 mg/L, 100 mg/L using hybrid corn silk as biosorbent

The results of maize (Zea mays L.) corn cob testing also showed that the % of Cd$^{2+}$ ion removal was highest from the initial concentration solution of 100 mg/L at pH 6 when it was 50%, while Ni$^{2+}$ showed that the highest % of removal of 34.8 % was from the initial concentration solution 40 mg / L at pH 6. (Figure 4.) Similar results were shown by the maize (Zea mays L.) corn silk biosorbent where it was shown that the highest efficiency for Cd$^{2+}$ ions is achieved at pH 6 and an initial concentration of 100 mg/L when 40% is removed. Ni$^{2+}$ ions with corn silk-based on the maize (Zea mays L.) as biosorbent showed the best results of all tested samples. They were removed in a percentage of as much as 80.9% and from a solution with an initial concentration of nickel ions of 40 mg /L at pH 3. (Figure 5.)
The initial concentration of metal ions is the driving force of the mass transfer process between the two phases (solid and aqueous), as well as the process of chemical binding of metal ions to the active centers. As the initial concentration increases, the degree of removal increases significantly while the removal efficiency decreases because the increased initial concentration of metal ions leads to competitive sorption at a constant number of available active binding sites on the biosorbent surface. [7] [8] This justifies the results obtained when it comes to Cd^{2+} ions where with an initial concentration of 100 mg/L the highest removal efficiency was achieved for all samples used, while when it comes to Ni^{2+} ions the highest removal efficiency was achieved at an initial concentration of 40 mg/L for all samples, while the maize (Zea mays L.) corn silk sample proved to be the best. On the other hand, pH value is the most important factor for the biosorption process because it affects the activity of pollutant ions in the solution as well as the activity of functional groups on the surface of the biosorbent. [9] At lower pH values, functional groups on the surface of the biosorbent are protonated, becoming positively charged, while with increasing pH, deprotonation occurs, where by functional groups become negatively charged and as such have the ability to interact with positively charged ions. [10] When it comes to the effect of pH on removal % for
used biosorbents for Cd$^{2+}$ ions the best removal % was at pH 6 while for Ni$^{2+}$ ions better removal % show at pH 3, where the physical and chemical properties of the metal (ionic radius, electronegativity, valence) play an important role in the efficiency of removal of the mentioned metals.

Examination of the morphology before and after the adsorption process showed significant differences in the structure of the biosorbents used. The photographs show the structure of the biosorbents used before the adsorption process, where larger cavities and pores within them that are specific for natural biometals, which originate from the preserved cellular structure and structure of plants, are clearly visible. [11] [12] After the adsorption process with Ni$^{2+}$ and Cd$^{2+}$ ions, a changed morphology compared to the morphology before the adsorption average occurs, which can be seen in the Figure 6. a) b) and Figure 7.a) b). Similar findings have been made by other researchers who have used natural biomaterials. [13] [14] [15]

These changes in the structure lead to the conclusion that sorption is associated with chemical changes on the surface of the biosorbent, which was confirmed by other researchers who used corn residues to remove heavy metal ions. [16]

One of the most well-known isotherms often used by adsorption-desorption analyzes is the Freundlich isotherm [17], which was also used in this paper, and its values are shown in Table 1. Otherwise, it is an empirical model describing adsorption on a heterogeneous surface. [18] $K_F$ is a parameter related to the binding capacity of the adsorbate, while the value of the constant $n$ indicates the affinity of the adsorbent for the adsorbate. A value of constant $n$ greater than 1 indicates that adsorption is favored [19]. Some authors cite the parameter $1/n$ as a heterogeneity factor, and the lower its value, the greater the heterogeneity [20], which was shown in our samples by the maize (Zea mays L.) corn cob.

Based on the data shown in Table 1., it can be seen that the value of the coefficient $1/n$ for the sample of hybrid corn cob as a biosorbent was obtained only for the process of biosorption of Cd$^{2+}$ ions at pH 3 while for other samples it was not possible to calculate the values of this parameter. Biosorption process did not occur or occurred in a negligible amount, while the value of the coefficient $1/n$ for the sample of hybrids corn silk was 2 for the sample of Cd$^{2+}$ ion biosorption at pH 3, which indicates the existence of high-energy sorption centers, and that adsorption is more pronounced at lower pH.
values. The value of 1/n for the biosorption of Cd ions at pH 6 was 0.696, which indicates the presence of sorption centers of approximately equal energy.

The results of the calculated values of the coefficient 1/n for biosorbent based on the maize (Zea mays L.) corn cob showed that it is a biosorbent of heterogeneous surface with moderate sorption intensity according to Ni$^{2+}$ and Cd$^{2+}$ ions, while for the biosorbent based on maize (Zea mays L.) corn silk all coefficient 1/n to a good sorption intensity according to the tested heavy metal ions and Ni$^{2+}$ and Cd$^{2+}$ where at pH 6 the value of 1/n was 0.4006 Ni$^{2+}$ and 0.754 Cd$^{2+}$.

**Table 1: Values of Freundlich adsorption isotherm constants for used biosorbents**

| Metal | The values of the Freundlich constants | pH | Hybrid corn cob | Hybrid corn silk | Zea mays L. corn cob | Zea mays L. corn silk |
|-------|----------------------------------------|----|----------------|----------------|--------------------|---------------------|
| Cd    | Kf                                     | 3  | -              | -              | -                  | -                   |
|       | 1/n                                    |    | 1.8323         | 2.0291         | 0.3861             | 1.5985              |
|       | R$^2$                                  |    | 0.8192         | 1              | 0.6149             | 1                   |
|       | Kf                                     | 6  | -              | 0.2058         | -                  | 0.2913              |
|       | 1/n                                    |    | -              | 0.696          | 3.4063             | 0.754               |
|       | R$^2$                                  |    | 0.9255         | 1              | 0.954              | 1                   |
| Ni    | Kf                                     | 3  | -              | 26.329         | -                  | -                   |
|       | 1/n                                    |    | -              | -              | -                  | -                   |
|       | R$^2$                                  |    | -              | -              | -                  | -                   |
|       | Kf                                     | 6  | 2.315          | 7.678          | 0.8523             | 0.6146              |
|       | 1/n                                    |    | -              | -              | 0.2653             | 0.4006              |
|       | R$^2$                                  |    | 1              | -              | 1                  | 1                   |

**IV. CONCLUSION**

The results of testing the possibility of using biomass based on two types of the maize – corn cob and corn silk for removing Cd and Ni ions showed that they can be used to remove Cd and Ni ions and that the highest percentage of removal of biosorbent based on corn cob was from a solution of initial concentration 100 mg/L for Cd$^{2+}$ ions at pH 3 when 32.4% were removed, while the highest removal percentage for Ni$^{2+}$ ions was from a solution of initial concentration 40 mg/L at pH 6 where the removal efficiency was 30%. The sample of biosorbent based on hybrid corn silk had the highest % removal for Cd$^{2+}$ ions 34.4% from a solution of initial concentration 100 mg/L at pH 6, and for Ni$^{2+}$ ions a solution of initial concentration 40 mg/L at pH 3 35.5%, while the maize (Zea mays L.) corn cob sample also had the highest % removal of Cd ions from the initial concentration solution 100 mg/L at pH 6 50%, and for Ni$^{2+}$ ions the largest % removal was from the initial concentration solution 40 mg/L at pH 6 34.8%. The maize (Zea mays L.) corn silk sample had the best removal efficiency for Cd$^{2+}$ ions from a solution with an initial concentration of nickel ions of 40 mg/L at pH 3.

Therefore, in the case of Cd$^{2+}$ ions, with an initial concentration of 100 mg/L, the highest removal efficiency was achieved for all samples used, while in the case of Ni$^{2+}$ ions, the highest removal efficiency was achieved at an initial concentration of 40 mg/L for all samples. Samples, while the maize (Zea mays L.) corn silk sample proved to be the best for the removal of these ions where the influence of pH has a great influence on the removal efficiency as well as the physico-chemical properties of the metal.

Morphological analysis of samples before and after the adsorption process showed significant differences in the structure of the biosorbents used, which lead to the conclusion that sorption is associated with chemical changes on the surface of the biosorbent.

The calculated values of the Freundlich isotherm parameters showed that the value of the coefficient 1/n for the hybrid corn cob sample as a biosorbent was the only value obtained for the Cd$^{2+}$ ion biosorption process at pH 3 while for other samples it was not possible to calculate, while the value of the coefficient 1/n was 2 for the sample of Cd$^{2+}$ ion biosorption at pH 3, which indicates the existence of high-energy sorption centers, and that the adsorption is more pronounced at lower pH values.
The results of the calculated values of the coefficient 1/n for biosorbent based on the maize (Zea mays L.) corn cob showed that it is a biosorbent of heterogeneous surface with moderate sorption intensity according to Ni and Cd ions, while the biosorbent based on the maize (Zea mays L.) corn silk all coefficient 1/n to a good sorption intensity according to the tested heavy metal ions and Ni and Cd where at pH 6 the value of 1/n was 0.4006 Ni²⁺ and 0.754 Cd²⁺.

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