REMOVAL OF Cu(II) AND Zn(II) IONS ON CORN COBS

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Chemical modeling of metal biosorption requires the characterization of biomass used as sorbent. The (local) structural environment of Cu(II) and Zn(II) sorbed on corn cobs biomass has been investigated by secondary electron microscopy (SEM) and energy-dispersive X-ray analysis (EDX). The IR spectrum obtained for the above said biomass render a complex nature of the corn cobs biomass. Despite this complexity some characteristic peaks may be identified and assigned, revealing the presence of hydroxyl, carboxyl, carbonyl and amino functional groups in the structure of investigated biomass. The paper also deals with studies of physical and biochemical properties of the sorbent: bulk density, apparent density, surface area, iodine number, CEC. From biomass characterization a possible mechanism of biosorption is suggested. The sorption experiments were carried out at a pH of 5.5 and low and high ionic strength in a 0.01M Na2SO4 solution. The results showed a high capacity of corn cobs with respect to the removal of the investigated metals cations.

INTRODUCTION

Biomass resulting from various natural or industrial sources may be used as complexing materials to remove heavy metals from wastewater.1 The accumulation of these metals by biomass and the major interaction mechanisms are based on ionic interactions and complex formation between metal cations and ligands contained in biomaterials.2-4

Biosorption of heavy metals is a promising technique for the removal of toxic metals from waste streams and is an alternative to conventional processes particularly attractive due to the low cost of sorbing material. The biosorption mechanisms are considered as being a metabolic independent one.3 The biomass content consists of polysaccharides, proteins, and lipids, offering many functional groups which can bind ions such as carboxyl, hydroxyl, carbonyl and amino groups.5-7

The purpose of this paper is to determine some characteristics of corn cobs biomass and the sorption mechanism of metal cations onto this biomass.

RESULTS AND DISCUSSION

The main characteristics of corn cobs are presented in Table 1 and Table 2.

Table 1  
Physical Properties of the Biomass

<table>
<thead>
<tr>
<th>Property</th>
<th>Values</th>
<th>Used Methods</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk Density</td>
<td>0.343 g cm⁻³</td>
<td>Standards 5388-80,5</td>
</tr>
<tr>
<td>Real Density</td>
<td>0.6372 g cm⁻³</td>
<td>Standards 5388-80,5</td>
</tr>
</tbody>
</table>

* Corresponding author: E-mail: simina_stefan_ro@yahoo.com
Table 1 (continues)

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
<th>Standard/Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Apparent Density</td>
<td>0.3016 g cm(^{-3})</td>
<td>Standards 5388-80,8</td>
</tr>
<tr>
<td>Porosity</td>
<td>52.66 %</td>
<td>Standards 5388-80,8</td>
</tr>
<tr>
<td>Specific surface area</td>
<td>52.98 m(^2) g(^{-1})</td>
<td>Standards 5388-80,8</td>
</tr>
<tr>
<td>Medium radius pore</td>
<td>173 Å</td>
<td>Froment F.G.,1979,9</td>
</tr>
<tr>
<td>CEC</td>
<td>0.7532 mmol g(^{-1})</td>
<td>Helfferich, F., 1962,10</td>
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</table>

Table 2
Biochemical Composition of the Biomass

<table>
<thead>
<tr>
<th>Type of biochemical compound</th>
<th>%</th>
<th>Used Methods</th>
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<tr>
<td>Cellulose</td>
<td>42.96</td>
<td>STAS 6840-73,11</td>
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<tr>
<td>Lignin</td>
<td>13.73</td>
<td>STAS 5338-90,12</td>
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<tr>
<td>Pentozans</td>
<td>21.50</td>
<td>STAS 6136-90,12</td>
</tr>
<tr>
<td>Raisins and waxes</td>
<td>6.25</td>
<td>STAS 6136-90,12</td>
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<tr>
<td>Proteins</td>
<td>4.01</td>
<td>N. Kjeldahl,</td>
</tr>
<tr>
<td>Ash</td>
<td>4.75</td>
<td>STAS 6949-73,14</td>
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<tr>
<td>Humidity</td>
<td>6.78</td>
<td>STAS 5388-80,8</td>
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</table>

IR spectrum

The IR spectrum of the natural biomass reflects the increased complex nature of sample. Despite this complexity some characteristic peaks may be assigned.

Taken into account the similarities presented in the literature, one may identify here the following functional groups:

- glicozidic C-O-C group presents characteristic absorption at 1163 cm\(^{-1}\);\(^{15-16}\)
- C=O stretching of the acidic group has a peak at 1648 cm\(^{-1}\);\(^{17}\)
- CH\(_3\)-COO- group has a peak at 1371 cm\(^{-1}\);\(^{16}\)
- amino group presents characteristic absorption at 3500-3000 cm\(^{-1}\) (3420 cm\(^{-1}\)) and at 1250 - 1000 cm\(^{-1}\);\(^{16-17}\)
- the strong band found at 1200 – 950 cm\(^{-1}\) (1032 cm\(^{-1}\)) may be assigned to an alchool stretching;\(^{16-17}\)
- bending vibration of OH in fenols is 1255 cm\(^{-1}\);\(^{15}\)
- bending vibration of CH\(_3\)-CH\(_2\)- and CH\(_3\)-in lignine is 1460 cm\(^{-1}\);\(^{15-16}\)
- bending vibration of C=C in aromatic rings is 1430 cm\(^{-1}\) and 1518 cm\(^{-1}\);\(^{16}\)
- bending vibration of –CH\(_2\)- is 2930 cm\(^{-1}\);\(^{16}\) The IR analysis showed that corn cobs has functional groups (carboxyl, hydroxyl, carbonyl, and amino) that retain metal cations from aqueous solutions.

Sorption isotherms

The Fig. 1 shows the variation of metal uptake with solution concentration at equilibrium. The maximum metal uptake capacity for the biomass is 0.253 mmol Zn(II) g\(^{-1}\) and 0.385 mmol Cu(II) g\(^{-1}\).

By comparing the isotherms of adsorption for Zn(II) and Cu(II) of biomass in the same initial conditions, at variable initial concentrations one observe the increasing of adsorption capacity with increasing of the initial heavy metal concentration. The biomass has a highly uptake capacity for Cu(II) than for Zn(II) the Fig. 1. The maximum amounts of heavy metal sorbed onto biomass varied in the following descending order: Cu(II) > Zn(II), respectively 0.385mmol Cu(II)/g biomass, 0.253mmol Zn(II)/g biomass.

The heavy metals sorption data were analyzed using Langmuir and Freudlich equations. Langmuir and Freudlich sorption parameters of biomass for each of the two metals were calculated by using least square fitting. The values are shown in Table 3.
Cu(II) and Zn (II) adsorption isotherm present a high Langmuir affinity character and may be described very well using the Langmuir equation.

**SEM and EDX analysis**

The results obtained in SEM and EDX analysis are presented in Figs. 2a, 2b, 3a and 3b. In Fig. 2a and Fig. 2b is presented the SEM analyses of cobs corn before the sorption experiments; (magnified by 700 times and 2000 times). In Fig. 3a and Fig. 3b is presented the SEM of biomass after the sorption of Cu(II) cations on biomass, (magnified by 700 times and 2000 times). One presents in Fig. 4 the X-Ray Spectrum after the sorption of Cu(II). In Fig. 2a and Fig. 2b one may see that biomass presents an uneven, compacted structure, crossed by large canals. In Fig. 3a and Fig. 3b one may notice a major modification of biomass structure. The number of channels crossing the biomass is higher. The structure of sorbent is uniform showing that some sort of chemical reaction occurred at the biomass surface. Fig. 4 shows the X-Ray Spectrum of the mineral composition of biomass brought in contact with Cu(II) synthetic solution proving that the biomass retains a high amount of copper.

### Table 3

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<tr>
<th>Cation</th>
<th>Isotherm type</th>
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<tr>
<td>Cu^{2+}</td>
<td>a_m</td>
<td>1.2575</td>
<td>b</td>
<td>0.5198</td>
<td>R^2</td>
<td>0.9952</td>
<td>0.6795</td>
<td>1.297</td>
<td>0.9754</td>
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<tr>
<td>Zn^{2+}</td>
<td>0.6724</td>
<td>0.5733</td>
<td>0.9976</td>
<td>0.5417</td>
<td>1.27048</td>
<td>0.9653</td>
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<td>Freudlich</td>
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<td>Cu^{2+}</td>
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<td>R^2</td>
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<td>Zn^{2+}</td>
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Using data acquired from the characterization study, we have proceeded to the next stage consisting in suggesting possible reactions and processes between the metal ions and the solid adsorbing surface. It appears that biosorption processes, based on ion exchange processes and surface complexation, represents the mechanism involved in this particular case. Similar findings regarding the above processes are also reported in.18

Biosorption is a complex process, particularly in cases when the sorbents are of a natural organic origin. Natural organic matter contains aromatic rings and aliphatic chains that host numerous carboxylic, phenolic, hydroxyl, carbonyl and alkoxyl groups.

Biosorption has two extremes: weak physical sorption and a strong chemical sorption and may involve strong electrostatic interactions between ions or dipoles and surfaces, including ion exchange type reactions, and complexation reactions. A typical sorption process may also involve exclusively weak intermolecular forces (physical adsorption) such as van der Waals interactions and dipole interactions.

Physical adsorption is the result of relatively light binding forces, being a reversible process. The characteristic reaction of physical adsorption is:

\[ \text{Bio} + \text{Me}^{2+} \leftrightarrow \text{BioMe}^{2+} \]  \quad (1)

Chemosorption processes involve strong binding of sorbate to the sorbent, resulting in most cases a change in chemical character of surface and sorbate. Chemosorption is the result of relatively strong binding forces (>30Kcal/Mol), and is characterized by high adsorption energies; the chemosorption may be defined
as a slow and reversible process and includes ion exchange reactions or irreversible complexation reactions.

\[
\text{Bio-COOH} + \text{Me}^{2+} \leftrightarrow \text{Bio-COO-Me}^{+} + \text{H}^{+} \quad (2)
\]

\[
\text{Bio-OH} + \text{Me}^{2+} \leftrightarrow \text{Bio-O-Me}^{+} + \text{H}^{+} \quad (3)
\]

Complexation is a reaction whereby heavy metals ions replace one or more coordinated water molecules in the co-ordination with other nucleophilic groups or ligands.\(^\text{20}\) Ligands that coordinate with Cu(II) and Zn(II) via oxygen donor atoms -COO-, -CO, -O-, -C-O-C-. Taking into account the experimental results, one has suggested various spatial configuration for this process (see Formula I-IV), depending on the functional groups involved in this complexation process. The proposed configurations are in agreement with similar findings presented in [2] and [22].

![Formula I](image1)

*Formula I – Type of complex involving phenolic and carboxylic functional groups on lignin Me = Cu or Zn*

![Formula II](image2)

*Formula II – Type of complex involving carboxylic functional groups on lignine Me = Cu or Zn.*

![Formula III](image3)

*Formula III – Type of complex involving hydroxyl functional groups on cellulose (adjacent fibres) Me = Cu or Zn.*

![Formula IV](image4)

*Formula IV – Type of complex involving carboxylic and carboxylic and hydroxyl functional groups on cellulose (same fibre) Me = Cu or Zn.*

**EXPERIMENTAL**

Homoionic aqueous solutions of Zn(II) and Cu(II) were prepared from sulphate salts of these metals (ZnSO\(_4\) \(\cdot\)7H\(_2\)O, CuSO\(_4\) \(\cdot\)5H\(_2\)O, p.a. Fluka). Concentrations of these stock solutions were verified by flame atomic absorption spectrometry using a SOLAAR 32 equipment. All metal solutions were further diluted to the required concentrations using double distilled water. Na\(_2\)SO\(_4\) was used as supporting electrolyte. In all sorption experiments the biomass concentration was \(C_B = 1\) g L\(^{-1}\).

**Biomass Characterization**

The bulk density as the weight unit of the carbon within the adsorber and was measured according to Standards 5388-80. The apparent density, defined as the biomass weight with respect to its total volume (including pore volume and interparticle voids, adjusted for the moisture content) was measured by picnometry using the mercury method. The specific surface area defined as the accessible area of the solid surface per mass unit of material, was measured using adsorption of methylene blue in liquid phase according to Standards 5388-80. Iodine number refers to the milligrams of 0.02 N iodine solution adsorbed during a standard test (5388-80). The iodine number is a measure of the volume present in pores from 10 to 28 Å in diameter.

The biochemical composition of biosorbents, presented in Table 2, was characterized in terms of proteins, carbohydrates, lignine, raisin, waxes, ash, and humidity. The amount of proteins has been determined using the Kjeldahl nitrogen method.

In order to present a qualitative and preliminary analysis of the main chemical groups present on the biomass, an IR analysis in solid phase was performed using KBr pellets technique on a SP IR-620, Jasco-2000 equipment in the range 4000-400 cm\(^{-1}\).

**Sorption Isotherms**

Isotherm curves for Cu(II) and Zn(II) sorption on corn cobs were determined at a thermostated temperature of 20.0 \(\pm\) 0.2°C. 50 mL of heavy metal solution with concentration ranging from 0.15 to 3.0 mmol L\(^{-1}\), were brought in contact for 8 h with 50 mg of every type of biomass subjected to investigation. The pH of the Cu(II) and Zn(II) solutions was maintained at 5.0 \(\pm\) 0.2 below the
precipitation threshold for these metals. The suspensions were shaken for 8 h until biosorption equilibrium was reached, then it was filtered, and the concentration of heavy metals was determined by atomic absorption spectroscopy for the initial and the final solution concentrations. The amount of the heavy metal uptake by corn cobs, as mmol metal/g dry sorbent, is calculated from the material balance:

\[ q = \frac{C_i V_i - C_e V_f}{m} \]  

Where: \( q \) is the metal uptake, mmol g\(^{-1}\), \( C_i \), ion concentration in the initial solution, mmol L\(^{-1}\), \( V_i \), initial volume of solution, L, \( C_e \), ion concentration at equilibrium in the final solution, mmol L\(^{-1}\), \( m \) = mass of dry biosorbent used, g.

**SEM and EDX Analysis**

Scanning electron microscopy images (SEM) were acquired using a HITACHI S2600N with EDX probe field emission secondary electron microscope at 5 kV beam potential.

**CONCLUSIONS**

In this paper were investigated the physical and biochemical properties of corn cobs biomass used as sorbent for the removal of Cu(II) and Zn(II) from synthetic wastewaters. The IR analysis showed that corn cobs has various functional groups such as carboxyl, hydroxyl, carbonyl, making available a high range of various processes for the retention heavy metals.

The maximum amounts of heavy metals sorbed onto the investigated biomass deducted from Langmuir isotherms are 0.385 mmol Cu(II) g\(^{-1}\) biomass and 0.253 mmol Zn(II) g\(^{-1}\) biomass. Cu(II) and Zn (II) adsorption isotherms have a high Langmuir affinity character, and obey the Langmuir equation.

SEM and EDX analysis present the microstructure of sorbent before and after contact with synthetic solution of Cu(II), revealing an uneven, compact structure crossed by large canals before the interaction with heavy metal solutions, and a major modification of biomass structure after being contacted with heavy metals. The number of canals crossing the biomass is higher than in the initial case. The structure of sorbent is uniform, proving that a chemical reaction occurred at the biomass surface.

The EDX presents an uniform distribution of Cu(II) on surface biomass granules, the sorption process being one of a Langmuir type. The X-Ray Spectrum proves that copper and zinc ions are retained onto the biomass.

**REFERENCES**