Potential of Maize Cobs for Removal Zn(II) and Ni(II) in Aqueous Systems

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In this study, the ability of maize cobs to bind Zn(II) and Ni(II) was investigated as a function of initial metal ions concentration, at pH = 7.5. Freundlich and Langmuir adsorption models expressed the sorption phenomena of metal ions on the maize cobs. The best results were obtained for Freundlich isotherms. On the bases of this study, it may be concluded that maize cobs can be used as low-cost sorbent, natural and abundant sources for the removal of metal ions from aqueous systems.

Keywords: heavy metal, maize cobs, adsorption, equilibrium, Freundlich and Langmuir isotherms

Heavy metal contamination exists in aqueous waste streams of many industries. These are not biodegradable and tend to accumulate in living organisms, causing various diseases and disorders.

Recently great effort has been contributed to develop new adsorbents and improve existing adsorbents like granular activated carbon, other adsorbents such as iron oxide coated sand, porous cellulose carrier modified with polyethyleneimine, iron coat granular activated carbon, chitosan and modified chitosan, etc. One of the exploitation is the use of natural wastes. The natural wastes are the materials that have the low cost, high availability, and no need for complicated regeneration process.

Rice straw, maize cobs, walnut expeller meal, peanut skins, wool, peanut hulls, sugar cane bagasse, waste tea leaves, exhausted coffee, coconut husks are some of the examples of the agricultural products and by-products used for removal of heavy metals from wastewater [1-8, 11, 12]. These materials are abundant in nature, or are a by-product or waste material from another industry [9].

The studies showed that the metal ions adsorption on the agricultural wastes and by-products is possible as a result of the interactions or coordination to functional groups present in natural protein, lipids and carbohydrates positioned on cell wall. The sorption rate of metal ions on the sorbent is affected by the factors such as the number of reactive sites on the substrate, the particle size of the sorbent is affected by the factors such as the number of reactive sites on the substrate, the particle size of the sorbent, the report metal ions - sorbent, experimental conditions [9].

Romania is an important maize producer, the surface cultivated being about 34% from arable surface of the country (the surface cultivated with maize in Romania is up to 74% from the surface cultivated with this cereal in EU). Maize cobs contain 38% cellulose, 46.5% hemicellulose, 9.65% lignin, 3% proteins and has been identified as new sorbent for removal of heavy metals in aqueous solutions.

Materials and methods
Preparation of sorbent
The maize cobs were washed with de-ionized water, cut in the small pieces, air-dried and powered in a grinder. The meal was sieved through a 500 µm mesh and then through 400 µm. The meal retained on the 400 µm was soaked in dilute nitric acid solution (2% v/v) overnight, rinsed with de-ionized water and air-dried.

2 g maize cob into a 100 mL solution of the metal ion was used in the experiments.

Preparation of test solutions
Initial concentration of 10, 20, 30, 40, 50, 60, 70, 80, 90, 100 mg/L of all the two metal ions test solutions was prepared.

The investigation was effectuated at pH of 7.5 and temperature of 30°C.

Adsorption studies
The sorbent was added in the test solutions, pH and temperature were fixed. Different samples were left to stand for 70 min. The samples were filtered rapidly and the metal ions concentrations in the filtrate was determined using spectrophotometer HACH DR/2010 (was used the Standard Methods for the Examination of Water and Wastewater).

All experiments were duplicated and showed differences of less than 5.0%.

Adsorption isotherms
The Langmuir and Freundlich models have been used to evaluate the sorption potential of adsorbent.

When a quantity of adsorbent (maize cob) is contacted with a given volume of a liquid containing an absorbable solute (metal ions), adsorption occurs until equilibrium is achieved. The equilibrium state is characterized by a certain solute concentration in the adsorbent (q) and an associated final solute concentration in the liquid phase (Cₐ).

The adsorption capacity of ions metal on the maize cobs was calculated by the following equation [10]:

\[ q = \frac{(C_0 - C_a)V}{m}, \text{mg/g} \]  

(1)

where:
- \( q \) = metal ions adsorbed by sorbent, mg/g;
- \( V \) = volume of metal solution, L;
- \( m \) = mass of maize cobs, g;
- \( C_0 \) = initial metal concentration, mg/L;
- \( C_a \) = metal concentration at equilibrium, mg/L.

Depending on the volume of solution, the initial solute concentration, the mass of sorbent used, the report C/q, relation between \( C_a \) and \( q \) can be expressed in the shape...
of mathematics, through the Langmuir (2) and Freundlich (3) isotherms:

\[ q = \frac{b \cdot q_m \cdot C_e}{1 + b \cdot C_e} \quad \text{or} \quad q = \frac{C_e}{b \cdot q_m} \quad \text{(2)} \]

\[ \log q_m = \log K + \left( \frac{1}{n} \right) \log C_e \quad \text{(3)} \]

where:

\[ q_m = \text{maximum metal uptake or maximum adsorption capacity, mg/g,} \]
\[ b = \text{adsorption equilibrium constant,} \]
\[ K = \text{Freundlich constant related to adsorption capacity of the sorbent,} \]
\[ 1/n = \text{Freundlich constant related to adsorption intensity of the sorbent.} \]

The values of \( K \) and \( 1/n \), from the Freundlich equation, can be obtained from the intercept and slope, respectively, of the linear plot of experimental data of \( C_e/q \) (mg/L) versus \( \log C_e \).

The values of \( q_m \) and \( b \), from the Langmuir equation, can be obtained from the intercept and slope, respectively, of the linear plot of experimental data of \( \log q_m \) versus \( C_e \) (mg/L).

All experiments were duplicated and showed differences of less than 5.0%.

Results and discussions

The adsorption of ions metal on the maize cobs is particle diffusion controlled and this can be effected by the following processes: diffusion of the ions metal from the solution to the film surrounding the particle, diffusion from the film to the particle surface, diffusion from the surface to the internal sites, and uptake [7].

The figures 1 and 2 show the effect of initial ions metal concentration on the removal of ions metal by maize cobs. The sorption capacities of the sorbent increased with increasing ions metal concentration while the adsorption yields of ions metal showed the opposite trend. When the initial ions metal concentration was increase from 10 to 100 mg/L the loading capacity increased from 4.55 to 36 mg/g, for \( \text{Zn}^{2+} \) ions, and from 5 to 41 mg/g, for \( \text{Ni}^{2+} \) ions, increasing the transfer driving force and therefore the rate...
at which metallic ion pass from the bulk solution to the particle surface. This would results in higher metallic ion adsorption. On a relative basis the percentage adsorption of metallic ion decreases as the initial ion metallic concentration increases, from 91 to 72%, for Zn$^{2+}$ ions, and from 100 to 82%, for Ni$^{2+}$ ions.

The linearized Freundlich and langmuir adsorption isotherms of maize cobs for zinc and nickel ions are shown in figure 3 and 4. The Langmuir and Freundlich constants are display in table 1. It was found that both the Langmuir and Freundlich isotherm models can adequately describe the adsorption data, but the correlation coefficient was bigger for Freundlich isotherm than for Langmuir isotherm. The higher value of K showed easy uptake of ions metal from aqueous solution, for nickel ions (13.31) the higher value than zinc ions (5.098) was obtained. The n value, which reflect the intensity of sorption, presents the opposite trend, but this constant was found high enough for separation, 0.573 for Zn(II), respectively 0.34 for Ni(II). The $q_m$ value was higher for Ni(II) than for Zn(II), and the large value of b (45 - 45.12) denote a strong bonding of ions metal occurred with maize cobs.

Conclusions

In this study, the ability of maize cobs to bind Zn(II) and Ni(II) was investigated as a function of initial metal ions concentration, at $pH = 7.5$. Freundlich and Langmuir adsorption models expressed the sorption phenomena of metal ions on the maize cobs. The best results were obtained for Freundlich isotherms. On the bases of this study, it may be concluded that maize cobs can be used as low-cost sorbent, natural and abundant sources for the removal of metal ions.

References

3. ADEYIGA, A., HU, L., GREER, T., Removal of metal ions from wastewater with natural wastes. School of Engineering and Technology, Hampton University, Hampton, VA 23668, 1996

Table 1
PARAMETERS OF FREUNDLICH AND LANGMUIR ISOTHERM MODELS

<table>
<thead>
<tr>
<th>Ions</th>
<th>Freundlich constants</th>
<th>Langmuir constants</th>
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<tbody>
<tr>
<td></td>
<td>$K$</td>
<td>$1/n$</td>
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<tr>
<td>Zinc</td>
<td>5.098</td>
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<td>Nickel</td>
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<td>0.33462</td>
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