# MAIZE BRAN AS A LOW-COST RESOURCE FOR Cu(II) IONS REMOVAL

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The paper discusses the results of a study emphasizing the practical usefulness of a low-cost agricultural resource, "maize bran", as sorbent for the removal of Cu(II) ions from wastewaters. To establish the optimum conditions of batch retention, the effect of initial solution pH, sorbent dose, initial concentration, time contact and temperature on Cu(II) sorption by maize bran has been studied. The kinetic description of the Cu(II)-maize bran sorption system was performed by the Lagergren pseudo-first-order equation. The equilibrium data at three different temperatures were processed according to Langmuir and Freundlich isotherm models. The Langmuir maximum sorption capacities were determined as 0.114, 0.132 and 0.149 mmol/g, at 4, 25 and 60 ºC, respectively. To evaluate the thermodynamic feasibility of the Cu(II) sorption process, free energy change ($\Delta G$), enthalpy change ($\Delta H$) and entropy change ($\Delta S$) have been calculated on the basis of the Langmuir constants. The obtained results suggest that maize bran sorption may be a progression towards the elaboration of a prospective method.

***Keywords***: maize bran, copper, sorption, kinetics, thermodynamics

## INTRODUCTION

The intensive development of electroplating, smelting, metal processing, machine manufacturing, organic synthesis and tanning industry resulted in a drastic increase in the amounts of copper entering the environment through industrial wastewaters. Unlike many other heavy metals, copper in trace amounts is beneficial to organisms. However, excessive amounts of Cu(II) can lead to serious health and environmental problems. Thus, Cu(II) in wastewaters is toxic to organisms and crops; for example, concentrations of 0.1-0.2 mg/L are lethal to fish.[1] Also, Cu(II) has a strong influence on the self-cleaning properties of water, which could inhibit the biological oxygen-consuming processes.[2]

The existing techniques developed for Cu(II) removal from wastewaters include chemical precipitation/neutralization, ion exchange, membrane separation, electrodialysis and activated carbon adsorption. All these methods suffer from the major drawback of secondary pollution. In this context, removal of Cu(II) ions from domestic and industrial wastewaters is now shifting from the use of conventional methods to the use of low-cost sorbents.[3-7] In recent years, many low-cost sorbents, such as thermal power plant ash,[8] spent-grain,[9] chestnut shell,[10] orange peel,[11] rice bran,[12] date stones and palm tree waste[13] and hemp[14,15] have been investigated for their sorption capacity towards Cu(II) ions.

Maize bran is a by-product of the commercial maize dry milling process. Maize bran contains heteroxylans (approximately 50%), cellulose (approximately 20%) and phenolic acids (approximately 4%, mainly ferrulic and diferrulic acids), starch (9-23%), proteins (10-13%), lipids (2-3%) and ash (2%).[16]

The idea of maize bran use as a heavy metal ion collector from aqueous solutions is based on the fact that it is economical, easily available and mostly biodegradable. Thus, maize bran has been found to be an environmentally friendly and potential low-cost sorbent for Pb(II)[17] and Cr(VI)[18] ions from aqueous solutions.

The aim of this work was to investigate the sorption potential of agricultural waste maize bran in the removal of Cu(II) ions from diluted aqueous solutions. The effect of different variables, such as the initial pH of solution, maize bran dose, Cu(II) concentration in solution, contact time and temperature on the sorption capacity of maize bran, has been studied. The Langmuir and Freundlich isotherm models were used to describe equilibrium data. Also, the sorption mechanisms of Cu(II) ions on maize bran were evaluated in terms of thermodynamics and kinetics.

## EXPERIMENTAL

### Sorbents and reagents

The maize bran used in these experiments, a by-product of a flour milling plant, was collected from a private company in Iaşi, Romania. The maize bran was dried at 105 °C and stored in a dessicator before use.

X-ray diffraction and IR studies of maize bran showed that, apart from various organic functional groups (–OH; –C=C–H; –C=O, aromatic ring), maize bran also contains metal oxides (of Al, Mn, Si, Fe and others) and carbon.[16]

A stock solution of 1037 mg/L was prepared by the dissolution of analytical reagent grade $CuSO_4 \cdot 5H_2O$ in deionised water, and then standardized gravimetrically. The working solutions of Cu(II) were prepared by appropiate dilutions of the stock solution.

To study the effect of medium acidity on the sorption process, a $10^{-2}$M concentrated $H_2SO_4$ solution has been used.

### Batch sorption studies

Batch sorption experiments for Cu(II) retention by maize bran were performed according to the procedure presented in Figure 1.

The sorption experimental conditions are systematized in Table 1.

### Equipment

- GBS Avanta 2007 Atomic Absorption Spectrometer with accessories, such as auto-sampler and furnace system;
- M-64 Radiometer pH-meter.

## RESULTS AND DISCUSSION

### Effect of initial pH

The solution pH is one of the most important parameters controlling the sorption capacity, due to its strong influence on the surface properties of the sorbent and ionic forms of copper. All experiments were performed in the initial pH range of 1-5, values that do not permit the chemical precipitation of Cu(II) as $Cu(OH)_2$. According to the speciation data from literature, over this pH range, the heavy metal ion under study exists in its double positively charged form.[19]

Contact of ca. 1 g maize bran samples with 50 mL aqueous solution containing definite amounts of metal ion

↓

Filtration of mixture

↓

Atomic absorption spectrometry of the final ion concentration in filtrate

↓

| Calculation of the parameters characteristic of the maize bran sorption process | |
|---|---|
| Sorption percentage, R% | Retained amount of Cu(II), q(mg/g) |
| $R\% = [(C_0 - C)/C_0].100$ | $q = [(C_0-C)/G].V$ |

where:
$C_0$ = initial concentration of metal ion (mg/L)
C = cation concentration in solution after sorption (mg/L)
V = volume of solution (mL)
G = mass of maize bran (g)

Figure 1: Scheme of Cu(II) sorption on maize bran under batch conditions

Table 1
Conditions of sorption studies

| Study of | Initial pH | Maize bran dose, mg/L | Cu(II) initial concentration, mg/L | Contact time, h | Temperature, ºC |
|---|---|---|---|---|---|
| Solution pH | 1-5 | 20 | 83 | 24 | 25 |
| Maize bran dose | 5 | 10-50 | 104 | 24 | 25 |
| Initial concentration | 5 | 20 | 20.8-145 | 24 | 25 |
| Contact time | 5 | 20 | 83-104 | 0.5-24 | 25 |
| Temperature | 5 | 20 | 20.8-145 | 24 | 4; 25; 60 |

Table 2
Influence of metal ion concentration in the initial solution on Cu(II) sorption by maize bran

| $C_0$, mg/L | q, mg/g | R, % |
|---|---|---|
| 20.8 | 1.04 | 73.00 |
| 41.7 | 2.20 | 68.00 |
| 63.0 | 2.67 | 57.65 |
| 83.0 | 3.87 | 45.60 |
| 104.0 | 4.66 | 44.20 |
| 124.0 | 5.58 | 41.08 |
| 145.0 | 6.28 | 40.24 |

Figure 2 shows the influence of pH on Cu(II) sorption from aqueous solutions by maize bran. It is obvious that the lowest amount of sorbed Cu(II) (0.23 mg/g) was found at pH = 1 (reached by acidification with $H_2SO_4$). However, with an increasing pH, sorption increases. The highest value of the Cu(II) amount retained on maize bran (3.95 mg/g) is observed at an initial pH of 5, in unbuffered solutions. Taking into account this behavior, the subsequent dependencies have been investigated from solutions with an initial pH of 5, performed by simple dilutions of the initial solutions.

The influence of pH on the batch sorption system under study might be explained by the nature of maize bran, which contains several metal oxides.[18] When mixed with a Cu(II) solution, these oxides undergo surface hydroxylation and form superficial hydroxyl species, which gives positively or negatively charged surfaces, as a result of subsequent acid–base dissociation. Thus, a low Cu(II) retention, corresponding to pH < 2, is probably caused by the repulsion between the maize bran surface with positive charge and the metal ion. As pH increases, the surface of maize bran becomes negatively charged. In this context, the increase of sorption with pH increasing in the 2-5 range might be due to these negative charges at the active sites on maize bran, which would allow chemisorption of the Cu(II) ions. These findings are in good agreement with the literature data reporting the effect of pH on heavy metal ions sorption by different types of natural and waste materials.[8,20]

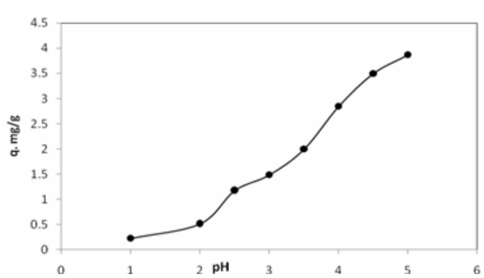


Figure 2: Effect of initial pH of solution on Cu(II)–maize bran batch sorption system: C = 83 mg/L, maize bran dose = 1 g, pH = 5

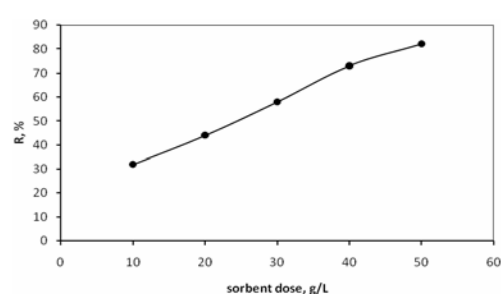


Figure 3: Effect of maize bran dose on percentage removal of Cu(II); C = 104 mg/L, pH = 5

**Effect of maize bran dose**

Figure 3, illustrating the influence of maize bran dose on Cu(II) sorption by maize bran, shows that the removal of Cu(II) increased with increasing the sorbent dose. This trend may be attributed to the increase in maize bran surface area and to the availability of more sorption sites.[21]

**Effect of initial concentration of Cu(II)**

The amount of Cu(II) retained on maize bran (q) increased with increasing metal ion concentration, while the Cu(II) sorption percentage decreased (Table 2). A higher initial concentration might be closely associated with the high values of the ratio between the initial number of Cu(II) mmoles and the limited number of available binding sites, resulting in an enhanced Cu(II) uptake. The occupation of the total active sites on maize bran hinders the access of Cu(II), consequently decreasing the sorption percentage. This behavior leads to the conclusion that maize bran as agricultural waste could be efficiently used in the removal of Cu(II) from wastewaters with low contents of the tested cation.

**Influence of contact time**

The effect of contact time on sorption of Cu(II) from solutions with initial pH of 5 and different initial concentrations is illustrated in Figure 4.

The kinetic curves plotted in Figure 4 show that, in the initial stages of sorption, the amounts of Cu(II) sorbed on maize bran increase sharply with increasing the contact time of phases, attaining values remaining almost constant.

To study the controlling mechanism of the Cu(II) sorption process on the tested maize bran, the pseudo-first-order equation was used to test the experimental data. The pseudo-first-order rate expression is given by the Lagergren equation:[22]

$$\log (q_e - q_t) = \log q_e - \frac{k_1}{2.303} \cdot t$$

where $q_e$ and $q_t$ are the amounts of cation (mg/g) sorbed at equilibrium and at time t, respectively, and $k_1$ is the pseudo-first-order sorption rate constant ($min^{-1}$). The kinetic parameters obtained from the linear Lagergren plots are given in Table 3. It is obvious from Table 3 that the kinetics of Cu(II) sorption on maize bran follows the Lagergren pseudo-first-order model.

Also, the data from Table 3 point out that Cu(II) initial concentration has a significant influence on the sorption rate. Thus, for an increase in Cu(II) initial concentration from 83 mg/L to 104mg/L, the values of the pseudo-first sorption rate increased from $2.3 \times 10^{-3}$ to $3.45 \times 10^{-3}$ $min^{-1}$, respectively.

**Sorption isotherms**

In order to successfully represent the dynamic sorption behavior, it is important to have a satisfactory description of the equilibrium state between the two phases forming the sorption system. The Langmuir and Freundlich sorption isotherms were tested to fit the experimental data.

The Langmuir sorption isotherm is given by the equation:[23]

$$q = \frac{K_L \cdot C \cdot q_0}{1 + K_L \cdot C}$$

where $K_L$ is a constant related to the sorption capacity and $q_0$ is the maximum capacity of sorption. The Langmuir equation assumes the formation of a monolayer coverage of Cu(II) at maize bran surface, containing a finite number of homogeneous sites of sorption. The Langmuir isotherms for Cu(II) retention on the low-cost sorbent under study at different temperatures are presented in Figure 5.

Table 4 characterizes Cu(II) sorption on maize bran by the Langmuir constants obtained from the corresponding linear Langmuir plots, and shows that the maize bran under study may be considered as a reasonable sorbent for Cu(II) ions removal from aqueous solutions.

Table 3
Kinetic description of Cu (II)–maize bran batch sorption system

| Cu(II) initial concentration, mg/L | Plot of linear regression equation | $R^2$ | $q_e$, (mg/g) | $k_1$, $min^{-1}$ |
|---|---|---|---|---|
| 83 | y = -0.001x + 0.428 | 0.984 | 3.59 | $0.23 \times 10^{-2}$ |
| 104 | y = -0.0015x + 0.532 | 0.993 | 4.66 | $0.345 \times 10^{-2}$ |

Table 4
Langmuir and Freundlich constants characteristic of Cu(II) sorption by maize bran

| T, K | Freundlich isotherm | | | Langmuir isotherm | | |
|---|---|---|---|---|---|---|
| | $K_F$ | n | $R^2$ | q (mg/g) | $K_L$ (L/mol) | $R^2$ |
| 277 | 1.33 | 2.24 | 0.977 | 0.114 | 469 | 0.987 |
| 298 | 1.97 | 2.28 | 0.974 | 0.132 | 624 | 0.974 |
| 333 | 2.33 | 2.40 | 0.970 | 0.149 | 964 | 0.972 |

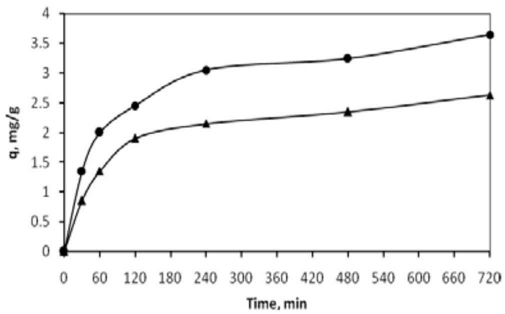


Figure 4: Influence of contact time on retention of Cu(II) by maize bran
(▲ C = 83 mg/L; • C = 104 mg/L)

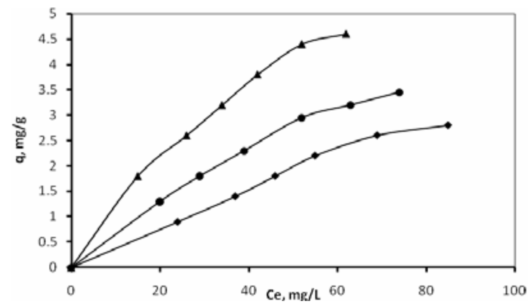


Figure 5: Langmuir isotherms for Cu(II) sorption on maize bran at different temperatures
(▲60 $^0$C; • 25 $^0$C; ♦ 4 $^0$C), pH = 5

The Freundlich equation can be described by the following linearised form:[24]

$\log q = \log K_F + (1/n) \log C$

where q is the amount of Cu(II) taken up per 1 g of maize bran (mg/g), C is the Cu(II) concentration left in the solution at equilibrium (mg/mL); $K_F$ and n are the Freundlich constants relating to the factors affecting the retention process: sorption capacity ($K_F$) and energy of sorption (n), respectively. The Freundlich equation is based on a logarithmic decrease in the enthalpy of sorption with the increase in the fraction of occupied sites. The values of the Freundlich constants for the maize bran–copper(II) sorption system are listed in Table 4. The n values are above unity, indicating a favorable sorption of copper by maize bran at all working temperatures. To compare the Langmuir and Freundlich isotherm models, the experimental data were statistically processed by linear regression. The high values of the linear regression correlation coefficients ($R^2$) for both Langmuir and Freundlich plots (Table 4) suggest that monolayer sorption, as well as heterogeneous surface conditions, can co-exist under the applied experimental conditions.

**Effect of temperature and thermodynamic parameters**

It is obvious from Figure 5 that temperature has a favorable effect within the sorption system under study. Both the Langmuir and Freundlich constants (Table 4) increase with increasing temperature, showing that the sorption capacity and the intensity of sorption are enhanced at higher temperatures. Furthermore, this trend indicates the endothermic and chemical nature of the studied cation sorption on maize bran.

For evaluating the thermodynamic feasibility of the Cu(II) sorption process and for confirming its nature, the thermodynamic parameters: free energy change ($\Delta G$), enthalpy change ($\Delta H$) and entropy change ($\Delta S$) have been calculated. Based on the values of the Langmuir sorption constant $K_L$ at different temperatures, the following equations have been used: [8]

$$\Delta G = - RT \ln K_L$$

$$\ln K_L = \text{constant} - \frac{\Delta H}{RT}$$

$$\Delta S = \frac{\Delta H - \Delta G}{T}$$

where R is the gas constant and T is the absolute temperature. The obtained data are presented in Table 5. The negative values of $\Delta G$ at all working temperatures validate the feasibiliy of the sorption process and the spontaneity of the Cu(II) retention by maize bran. The positive value of $\Delta H$ shows the endothermic nature of the Cu(II) sorption process, favored by the temperature increase.

The positive value of entropy change suggests the increase in randomness at the solid–liquid interface during sorption of Cu(II) on maize bran.

Table 5
Thermodynamic description of Cu(II) sorption by maize bran

| T, K | ΔG, kJ/mol | ΔH, kJ/mol | ΔS, J/mol.K |
|---|---|---|---|
| 277 | -14.16 | | 0.076 |
| 298 | -15.92 | 6.897 | 0.076 |
| 333 | -19.01 | | 0.077 |

## CONCLUSIONS

The maize bran collected from a private company in Iasi, Romania, may be described as a reasonable sorbent for the Cu(II) ions from diluted aqueous solutions. Within the pH range under study (1-5), sorption increases when increasing the initial pH of the solution. In this context, all experiments were performed at an initial pH of 5 in unbuffered solutions. The removal of Cu(II) increased with increasing the maize bran dose. The amount of Cu(II) retained on maize bran increases with increasing the initial concentration of Cu(II), while the Cu(II) sorption percentage decreases. The kinetics of Cu(II) sorption on maize bran is described well by the Lagergren pseudo-first-order model. Cu(II) sorption on the tested maize follows both Langmuir and Freundlich isotherm models. The obtained values of the isothermal thermodynamic parameters show that Cu(II) retention is a spontaneous process of endothermic and chemical nature.

## REFERENCES

[1] P. Subhashree and L. C. Rai, *J. Microbiol*., **17**, 829 (2001).
[2] P. Kaewsam, *Chemosphere*, **47**, 1081 (2002).
[3] N. A. Khan, S. Ibrahim and P. Subramaniam, *Malaysian J. Sci*., **23**, 43 (2004).
[4] J. C. Igweandi and A. A. Abia, *African J. Biotechnol*., **5**, 1167 (2006).
[5] H. K. Alluri, S. R. Roncha, V. S. Setalluri, Y. S. Bondili, V. Suryanaraya and P. Venkateshwar, *African J. Biotechnol*., **6**, 2824 (2007).
[6] D. Sud, C. Mahajan and M. P. Kaur, *Bioresource Technol*., **99**, 6017 (2008).
[7] R. M. Gligor and M. Gavrilescu, *Env. Eng. Manag. J*., **8**, 353 (2009).
[8] L. Tofan, C. Păduraru, D. Bîlbă and M. Rotariu, *J. Hazard. Mater*., **156**, 1 (2008).
[9] S. Lu and S. W. Gibb, *Bioresource Technol*., **99**, 1509 (2008).
[10] Z.-Y. Yao, J.-H. Qi and L.-H. Wang, *J. Hazard. Mater*., **174**, 137 (2010).
[11] N. C. Feng, X. Y. Guo and S. Lang, *J. Hazard. Mater*., **164**, 53 (2009).
[12] X. Wang and Y. Qim, *Process. Biochem*., **40**, 677 (2005).
[13] Z. Belala, M. Jeguirim, M. Belhachemi, F. Addoun and G. Trouve, *Env. Chem. Lett*., DOI:10.1007/s10311-009-0247-5.
[14] C. Păduraru and L. Tofan, *Cellulose Chem. Technol*., **36**, 375 (2002).
[15] L. Tofan and C. Păduraru, *J. Balkan Ecol*., **2**, 106 (1999).
[16] E. Carvajal-Millan, A. Rascon-Chu, J. A. Marquez-Escalante, V. Micard, N. Ponce de Leon and A. Gadea, *Carbohydr. Polym*., **69**, 280 (2007).
[17] K. K. Singh, M. Talat and S. H. Hasan, *Bioresource Technol*., **97**, 2124 (2006).
[18] S. H. Hasan, K. K. Singh, O. Prokash, M. Talat and Y. S. Ho, *J. Hazard. Mater*., **152**, 356 (2008).
[19] E. Fergusson, in "The heavy elements chemistry, environmental impact and health effect", Pergamon Press, New York, 1990, p. 400.
[20] H. Aydin, Y. Bulut and C. Yerlikaya, *J. Env. Manag*., **87**, 37 (2008).
[21] J. A. Hefne, W. K. Mekhemer, N. M. Alandis, O. A. Aldayel and T. Alajyan, *Int. J. Phys. Sci*., **3**, 281 (2008).
[22] S. Lagergren, *Handlinger*, **24**, 1 (1898).
[23] I. Langmuir, *J. Am. Chem. Soc*., **38**, 2221 (1916).
[24] H. M. Freundlich, *Z. Phys. Chem*., **57**, 385 (1906).