

## SCAVENGING CADMIUM, COPPER, LEAD, NICKEL AND ZINC IONS FROM AQUEOUS SOLUTION BY MODIFIED CELLULOSIC SORBENT

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The adsorption of Cd, Cu, Pb, Ni and Zn ions on maize (*Zea mays*) stalk meal was examined by equilibrium studies at 29°C. The amounts of the metal ions removed from solution depended on the metal ion type, the ionic size of the metals and were enhanced by EDTA (%N=12.05) modification of the cellulosic sorbent. The sorption coefficient,  $K_d$ , of the metal ions between the absorbent phase and the bulk aqueous phase was found. The sorption data fitted the Langmuir isotherm equation and the maximum metal ion binding capacities,  $X_m$  of 20.5 mg g<sup>-1</sup> and 9.2 mg g<sup>-1</sup> for Cd (II), and of 12.2 mg g<sup>-1</sup> and 7.0 mg g<sup>-1</sup> for Cu (II) on EDTA modified and unmodified maize stalk meal were determined. This modification amounts to an increase of 44.87% and 57.38% for Cd (II) and Cu (II) ions adsorbed respectively. Ni (II), Zn (II) and Pb (II) ions showed  $X_m$  of 2.5 mg g<sup>-1</sup>, 4.3 mg g<sup>-1</sup> and 20.3 mg g<sup>-1</sup> for the unmodified sorbent respectively. The sorption on the unmodified sorbent of lead ions from solutions containing zinc ions shows that lead ions are preferentially removed from solution.

**Key words:** Sorption coefficient, Metal ions, Langmuir isotherm equation.

### Introduction

There has been considerable interest in recent times in the potential health hazards presented by heavy metals in the environment. Several workers (Roberts and Rowland 1973; Ferguson and Babela 1974; Burba and Willmer 1983; Ndiokwere 1983; Okieimen *et al* 1985) have reported on the level of accumulation of heavy metal in the environment and on materials that may be useful and economical in reducing the environmental load of these metals (Freidman *et al* 1973; Roberts and Rowland 1973; Kumar and Dara 1981; Burba and Willmer 1983; Okieimen *et al* 1985; Okieimen *et al* 1991). In continuation of the search for efficient and cost effective treatment, technologies have focused attention on the metal binding capacities of various biologically derived materials that can be procured at low cost, yet have adsorption capacities near those of commercial ion exchange resins.

In this study, maize (*Zea mays*) stalks, an agricultural by-products have been used as a sorbent for the removal of cadmium, copper, lead, nickel and zinc ions from aqueous solution.

### Materials and Methods

Maize stalks were obtained from farms within the campus of the University of Benin, Benin City, Nigeria. They were cut into small pieces, air-dried and powdered in a grinder. The maize stalk meal obtained was sieved through a 300 µm mesh screen. The portion of the maize stalk meal retained on the screen was used for the sorption.

**Modification of maize stalk meal.** A 20 g sample of the maize stalk meal was hydrolysed with 15 times its weight of 7% v v<sup>-1</sup> aqueous sulphuric acid for 24 h at 65°C. The mixture was filtered and the residue was washed thoroughly with deionised water and dried 50°C. A mixture of 17 g of the solid residue, 300 ml of pyridine and 56.7g of ethylene-diamine tetra acetic acid (EDTA) was heated under reflux for 3 h. The reaction mixture was cooled, diluted with 30 ml of deionised water and filtered. The EDTA modified husk was washed with deionised water until free of pyridine odour and then air dried. The nitrogen contents of both the unmodified EDTA-modified maize stalk meal were determined by the Kjeldahl method to be 6.44% and 12.05% respectively.

**Sorption of metal ions on the maize stalk meal.** Equilibrium sorption of Cd (II) and Cu (II) ions on EDTA-modified and of Pb (II), Ni (II) and Zn (II) ions on unmodified stalk meal from aqueous solution of their nitrate salts was examined at 29°C using various initial concentrations of the metal ions. In a typical experiment, 1 g of the cellulosic sorbent was dispersed in 100 ml of aqueous solution of metal ion of known initial concentration. The mixture was continuously shaken in a well stoppered flask for 1 h at room temperature (29°C). The mixture was filtered and the residual concentration of the metal ion in the filtrate was determined chelatometrically. The amount of the metal ion removed from solution by the husk was taken as the difference between the initial and residual concentrations of the metal ion (making corrections for the amount of metal ion contained in the volume of the metal ion solution retained in the cellulosic sorbent).

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Sorption of Pb (II) ions on the unmodified husk in packed columns was examined using various volumes of the metal ions solution of known initial concentration. Pieces of glass pipe (0.5 cm i.d x 35 cm long) were used for packed volumes. The glass pipe was narrowed down at one end. This end of the pipe was packed with glass beads to prevent the sorbent from falling out. 5 g of the stalk meal was placed dry in the column and the column was tapped gently to promote even distribution of packing. Glass beads were added on top of the packing to prevent the sorbent particles from floating and separating. The packing was wetted with slow water flow and was equilibrated for 4 h with static deionised water (Randall *et al* 1978). Flow of metal ions solution through the column was by gravity and was controlled (1 ml min<sup>-1</sup>) by a valve at the bottom of the column. The fraction of the Pb (II) ions removed from the solution by the stalk meal that was recoverable with dilute (2% v v<sup>-1</sup>) nitric acid was determined. Air-dried samples (1-2g) of the husk containing a known amount of the metal ion were treated with 50 ml of the dilute acid in a column. The amount of Pb (II) ions leached from the husk was determined chelatometrically.

## Results and Discussion

**Sorption capacity.** The variation in the levels of metal ion uptake by the stalk meal with initial metal ion concentration is shown in Table 1. It can be seen that the metal ions removed from solution is highest for Pb (II) ion and lowest for Ni (II) ions. The order observed is Pb (II) > Cd (II) > Zn (II) > Cu (II) > Ni (II). The differences in the amount of metal ions removed from solution by the cellulosic sorbent can be explained in terms of the difference in the ionic size of the metals, the metal ion type, the nature and distribution of the active groups on the cellulosic sorbent and the mode of interaction of the metal ions with the sorbent (Freidman *et al* 1973).

The influence on the sorption of Pb (II) ions of pH of the metal ion solution is also shown in Table 1. It can be seen that the levels of Pb (II) ions uptake are significantly reduced as the pH of the metal ion solution is reduced from about 6.0 to 2. Lead nitrate in aqueous solution and in the absence of complexing agents gives divalent lead ions. In the presence of excess chloride, chloride compounds of lead with oxidation number greater than two may be formed. The changes in the ionic radius associated with the formation of such chloride compounds would explain the reduction in the uptake of Pb (II) ions at low pH. Besides, the mechanism of interaction of metal ions with the sorbent suggested that sorption occurs primarily by preferential solubilisation of the metal ions (Freidman *et al* 1973). It may therefore be expected that a reduction in pH of the solution may lead to changes in the nature of the active sites, which acting independently or in conjunction with changes in the oxidation states of Pb (II) ions may reduce the solubilisation process by the sorbent. The pH dependence of the uptake of Pb (II) ions by maize stalk meal suggests that quantitative recovery of adsorbed metal ions can be achieved in acid medium.

The results in Table 1 also shows the effect of EDTA modification on the uptake levels of Cd (II) and Cu (II) ions on maize stalk meal. It is thought that EDTA moieties get incorporated on the meal during the modification process. The enhanced levels of metal ion uptake associated with EDTA modification could therefore be explained in terms of the increased number and type of reactive groups on the cellulosic substrate which can interact with the metal ions. It has been established that EDTA modification is associated with large increase of up to 100% in the nitrogen content of the modified material (Okieimen and *et al* 1991). The uptake of metal ions by unmodified cellulosic

**Table 1**

Equilibrium sorption of metal ions from aqueous solutions on maize stalks meal at 29°C using 100 ml of the metal ion solutions. pH of the metal ion solution is 6.2 approximately

Initial concentration (mg 100 ml <sup>-1</sup> )	Amount of metal ions adsorbed (mg g <sup>-1</sup> substrate)				
	Cd (II)	Cu (II)	Pb (II)	Ni (II)	Zn (II)
10.00	1.5 <sup>c</sup> ; 2.1 <sup>b</sup>	1.0 <sup>c</sup> ; 1.6 <sup>b</sup>	2.9 <sup>c</sup> ; 1.7 <sup>a</sup>	0.9 <sup>c</sup>	1.7 <sup>c</sup>
20.0	2.4 <sup>c</sup> ; 3.5 <sup>b</sup>	1.7 <sup>c</sup> ; 2.8 <sup>b</sup>	4.6 <sup>c</sup> ; 2.1 <sup>a</sup>	1.4 <sup>c</sup>	1.8 <sup>c</sup>
30.0	3.3 <sup>c</sup> ; 4.8 <sup>b</sup>	2.3 <sup>c</sup> ; 3.6 <sup>b</sup>	9.6 <sup>c</sup> ; 3.1 <sup>a</sup>	1.6 <sup>c</sup>	2.0 <sup>c</sup>
40.0	4.6 <sup>c</sup> ; 5.1 <sup>b</sup>	2.6 <sup>c</sup> ; 4.3 <sup>b</sup>	10.8 <sup>c</sup> ; 3.7 <sup>a</sup>	1.7 <sup>c</sup>	2.1 <sup>c</sup>
50.0	5.1 <sup>c</sup> ; 5.4 <sup>b</sup>	3.3 <sup>c</sup> ; 4.5 <sup>b</sup>	11.2 <sup>c</sup> ; 4.6 <sup>a</sup>	1.7 <sup>c</sup>	2.1 <sup>c</sup>

a) Uptake of Pb (II) ions from 0.01M HCl solution at pH of 2; b) Uptake levels by EDTA modified cellulosic sorbent; c) Uptake levels by unmodified cellulosic sorbent.



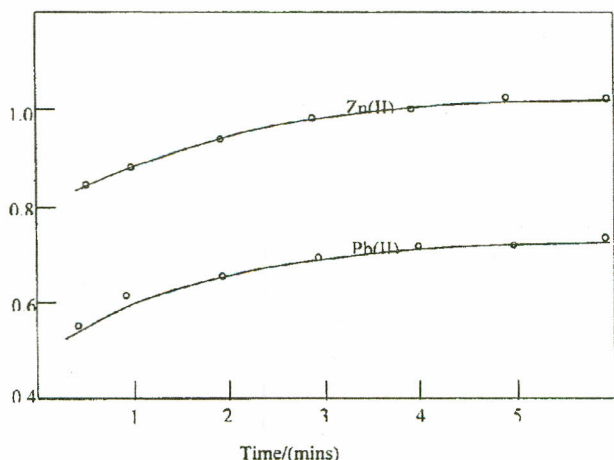


Fig 1. Uptake of Pb (II) and Zn (II) ions by maize stalk meals from solutions containing the metal ions mixed in a 1:4 ratio at 29°C.

materials from solutions containing a mixture of Pb (II) and Zn (II) ions (1:4) is shown in Fig 1. The results show that between 34% and 42% of the total amount of metal ions in solutions is removed by the cellulosic sorbent. It can be seen that although the Zn (II) ions removed from solution is 60% of the total amount of metal ions adsorbed, only about one third of the Zn (II) ions present in solutions is removed, whereas more than 75% of the Pb (II) ions in solution are removed by the sorbent. The relative uptake of the metal ions from solution containing Pb (II) and Zn (II) ions mixed in various proportions when sorption equilibrium is attained is shown in Table 2. The results show that irrespective of the relative amounts of the metal ions present in solution, Pb (II) ions are generally more efficiently removed from solution than Zn (II) ions by maize stalk meals. These results suggest that maize stalk meals may be useful in the selective removal of Pb (II) ions from waste waters (such as mining effluents) contaminated by Pb (II) and Zn (II) ions.

**Sorption coefficient.** Separation data of sorption processes may be expressed in terms of the distribution or sorption coefficient,  $K_d$ , which may be defined as the concentration of the adsorbate in the adsorbent phase divided by the concentration in the bulk-liquid phase. The value of  $K_d$  is of practical significance in the treatment of heavy metals laden waste waters with maize stalk meal. Primarily, it allows the determination of the number of cycles of equilibrium sorption processes required to reduce the levels of metal ions in aqueous effluents to acceptable levels.

Table 3 shows the sorption coefficient,  $K_d$  of the metal ions on the cellulosic sorbent. The results show that the concentration of the metal ions at the sorbent-water inter-

face is markedly higher than the concentration in the bulk aqueous phase. A relatively high  $K_d$  values was obtained from this study. This shows that the treatment of aqueous effluents contaminated at moderate levels (500 ppm) with heavy metals, would require a fairly small number of equilibrium sorption-cycles, to quantitatively reduce the metal ions to acceptable levels.

The values of sorption coefficient,  $K_d$ , could either be high or low. A low  $K_d$  value indicates that the metal ions has little tendency to adsorb onto the sorbent, will be highly mobile and may easily be leached from the adsorbent. This, therefore indicates that several equilibrium sorption cycles would be required in the treatment of heavy metals polluted effluents. On the other hand, a high  $K_d$  value indicates greater adsorption effectiveness, resulting in a small number of equilibrium sorption cycles.

**Sorption isotherm:** Sorption data usually follows Freundlich or Langmuir isotherms (Okieimen and Orhorhoro 1986). The two classical isotherms can be mathematically represented as:

$$\frac{x}{m} = KCe^{1/n} \dots\dots\dots (1)$$

$$\frac{Ce}{(x/m)} = \frac{1}{bXm} + \frac{Ce}{Xm} \dots\dots\dots (2)$$

Table 2

Sorption of Zn (II) ions from aqueous solution (100 ml) containing various Pb (II) and Zn ion mixed in various proportions by Maize stalk meal (0.5g) at 29°C, Total metal ion concentration (2 mg 100 ml<sup>-1</sup>)

Initial concentration Zn (II) ions (mg 100 ml <sup>-1</sup> )	Final concentration of Zn (II) ions (mg 100 ml <sup>-1</sup> )	Fraction of Zn (II) ions adsorbed (Mg)	Fraction of Pb (II) ions adsorbed (mg g <sup>-1</sup> )
1.6	1.1	0.3	0.8
1.0	0.7	0.3	0.8
0.5	0.4	0.3	0.8

Table 3

Distribution coefficient,  $K_d$ , of metal ions at 29°C

Metal ion	Equilibrium concentration of metal ions (mg g <sup>-1</sup> )	Distribution coefficient, $K_d$
Cd (II)	0.062-0.426(0.058-0.402)	24.19-12.11(36.20-13.43)
Cu (II)	0.068-0.401(0.072-0.396)	14.70-8.23(22.22-11.36)
Pb (II)	0.079-0.521	36.71-21.50
Ni (II)	0.071-0.201	12.06-8.84
Zn (II)	0.081-0.301	20.98-6.97

Data on EDTA modified sorbent in parenthesis.

- While  $X$  = amount of adsorbate removed from solution (mg)  
 $m$  = mass of adsorbent (g)  
 $K, n$  = Freundlich constants (coefficient and exponent of the isotherm respectively)  
 $C_e$  = equilibrium (residual) concentration of adsorbate ( $\text{mg l}^{-1}$ )  
 $b$  = constant related to the energy of adsorption  
 $X_m$  = maximum adsorption capacity ( $\text{mg g}^{-1}$  adsorbent)

If sorption followed the Freundlich isotherm, then, the plot of  $\log(X m^{-1})$  versus  $\log C_e$  would be linear from which  $k$  and  $n$  values could be calculated from the intercept and slope respectively. Alternatively, if sorption followed the Langmuir isotherm, then a linear relationship would be obtained between  $C_e x^{-1} m^{-1}$  and  $C_e$  from which the constant,  $b$  and  $X_m$  could be calculated.

Equation (2) predicts that  $X_m$  can be deduced from the slope of the linear plots of  $(x m^{-1})$  against  $C_e$ . When experimental data fit the Langmuir isotherm equation, a relative index of binding capacity is the apparent equilibrium constant,  $K$ , of the sorption process which may be obtained as the products of the values  $X_m$  and  $b$ . The data from this study fitted the Langmuir-isotherm equation. From the slopes of such plots of the data in Table 1. The maximum metal-ion binding capacities,  $X_m$ , of  $20.5 \text{ mg g}_1^{-1}$  and  $9.2 \text{ mg g}^{-1}$  for Cd (II) and of  $12.2 \text{ mg g}^{-1}$  and  $7.0 \text{ mg g}^{-1}$  for Cu (II), on EDTA modified and unmodified maize stalk meal respectively. This modification results in an increase in the binding capacity of the sorbent to about 44.87% for Cd (II) and 57.38% for Cu (II) ions. Ni (II), Zn (II) and Pb (II) ions showed  $X_m$  of  $2.5 \text{ mg g}^{-1}$ ,  $4.3 \text{ mg g}^{-1}$  and  $26.8 \text{ mg g}^{-1}$  for the unmodified sorbent respectively.

## Conclusion

This study generally showed that maize stalk, an agricultural by-product of no commercial value is an effective biosorbent and may be useful in scavenging traces of

heavy metals from waste waters. A packed column of the biosorbent also has a high potential for success as a solvent pre-concentration technique.

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