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REMOVAL OF Zn(II), Cd(II) AND Mn(II) FROM AQUEOUS SOLUTIONS BY ADSORPTION ON MAIZE STALKS

(Penyingkiran Zn(II), Cd(II) Dan Mn(II) Daripada Larutan Akueus Melalui Penjerapan Pada Tangkai Jagung)

G. O. El-Sayed[1]*, H. A. Dessouki [1] and S. S. Ibrahiem[2]

[1] *Chemistry Department, Faculty of Science, Benha University, Benha, Egypt*
[2] *National Water Research Center, Central Lab. for Environ. Qual. Monit., Elqanater Elkhayria, Egypt*

**Corresponding author: gamaloelsayed@yahoo.com*

Abstract

The potential to remove Zn(II), Cd(II) and Mn(II) from aqueous solutions through biosorption using maize stalks as an agriculture waste, was investigated in batch experiments. Different factors influencing metal adsorption such as contact time, initial metal ion concentration (40–1000 mg/L), pH (1–8), ionic strength and temperature (298–328 K) were investigated. The adsorption process was relatively fast and equilibrium was established after about 90 min. The optimum initial pH for zinc, cadmium and manganese adsorption by maize stalks was 7.0, 6.0 and 5.0, respectively. Under optimum conditions, the maximum adsorption capacity of zinc, cadmium and manganese ions was 30.30, 18.05 and 16.61 mg metal/g dry biomass, respectively. In order to investigate the sorption isotherm, three equilibrium models, Langmuir Freundlich and Temkin isotherms, were analyzed. The adsorption process for the three metal ions was found to be exothermic in nature. Free energy of adsorption (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) changes were calculated.

Keywords: maize stalks; metal removal; cadmium; manganese; zinc

Abstrak

Potensi penyingkiran Zn(II), Cd(II) dan Mn(II) daripada larutan akueus melalui bioerapan menggunakan tangkai jagung sebagai buangan pertanian telah dikaji menggunakan kaedah kelompok. Pelbagai factor yang mempengaruhi jerapan logam seperti masa sentuhan, kepekatan awal logam (40–1000 mg/L), pH (1–8), kekuatan ion dan suhu (298–328 K) telah dikaji. Proses penjerapan adalah agak pantas dan keseimbangan dicapai selepas 90 min. pH optimum bagi penjerapan zink, kadmium dan mangan oleh tangkai jagung masing-masingnya ialah 7.0, 6.0 dan 5.0. Pada keadaan optimum, muatan pejerapan maksimum bagi ion zink, kadmium dan mangan, masing-masing adalah 30.30, 18.05 and 16.61 mg logam/g biojisim kering. Bagi kajian isoterma erapan, tiga model keseimbangan iaitu isoterma Langmuir Freundlich dan Temkin dianalisis. Proses jerapan bagi ketiga-tiga ion logam adalah eksotermal. Perubahan tenaga bebas penjerapan (ΔG^0), entalpi (ΔH^0) dan entropi (ΔS^0) telah dikira.

Kata kunci: tangkai jagung; penyingkiran logam; cadmium, mangan; zink

Introduction

Toxic heavy metal contamination of industrial wastewater is an important environmental problem. Many industries such as electroplating, pigments, metallurgical processes, and mining and leather industries release various concentrations of heavy metals. Metal ions such as cadmium, chromium, copper, lead, zinc, manganese and iron are commonly detected in both natural and industrial effluents. The commonly used procedures for removing metal ions from effluents include filtration [1], chemical precipitation [2], chemical coagulation [3], flocculation [4], ion exchange [5], reverse osmosis [6], membrane technologies [7-9] and solvent extraction [10]. These processes may be ineffective or expensive, especially when the heavy metal ions are present in high concentrations. The use of adsorbents of biological origin has emerged in the last decade as one of the most promising alternatives to conventional heavy metal management strategies. Biosorption is a fast and reversible reaction of the heavy metals with biomass. The by-products obtained from biomaterial production are a cheap source of biosorbents. Several agricultural waste materials have been studied and developed for the effective removal of heavy metals like maize bran [11], coffee husks [12], rice straw [13], sugar peat pulp [14], olive pomace [15], apple wastes [16], palm kernel fibre [17], peanut hull [18], cocoa shell [19], hazelnut husks [20], oak sawdust [21] and grape stalks [22].

Maize is an economical crop in Egypt, large areas are cultivated with it. The aim of the present study is to examine the ability of maize stalks as cheep bio-adsorbent for removal of Zn(II), Cd(II) and Mn(II) ions from aqueous solutions. The different factors affecting adsorption process were evaluated as time of contact, initial concentration of the metal, solution pH, temperature and adsorbent dosage. Furthermore, equilibrium, kinetic and thermodynamic studies on the adsorption of different metal ions onto the maize stalks were also carried out for the design of adsorption process. The advantage of using maize stalks as adsorbent is the ability of using the dry biomass after removal process in the manufacture of a sheep type of artificial wood by special treatment.

Materials and Methods

Biomass preparation

Maize stalks were collected and used as sorbent for the biosorption of Zn(II), Cd(II) and Mn(II) ions. The maize stalks sample was collected from Sharqiya Governorate region of Egypt. Samples were washed several times using deionised water to remove extraneous and dust. They were then dried in an oven at 105 ºC for 24 h. The dried biomass was chopped and filtered. The granules were sieved and the particles having sizes less than 150 μm were used in the tests. The adsorbent was kept dry in a closed container until the time of use.

Determination of point of zero charge

Point of zero charge of an adsorbent surface is the pH at which that surface has a net neutral charge. This value was evaluated by adding 0.1g of maize stalks to 50 mL of water with varying pH from 2 to 11.6 and stirred for 24 h. The initial pH was adjusted by adding either HCl or NaOH solutions and the final pH of the solution was plotted against the initial solution pH (Figure 1). pHZPC for maize stalks is determined as pH 5.2.

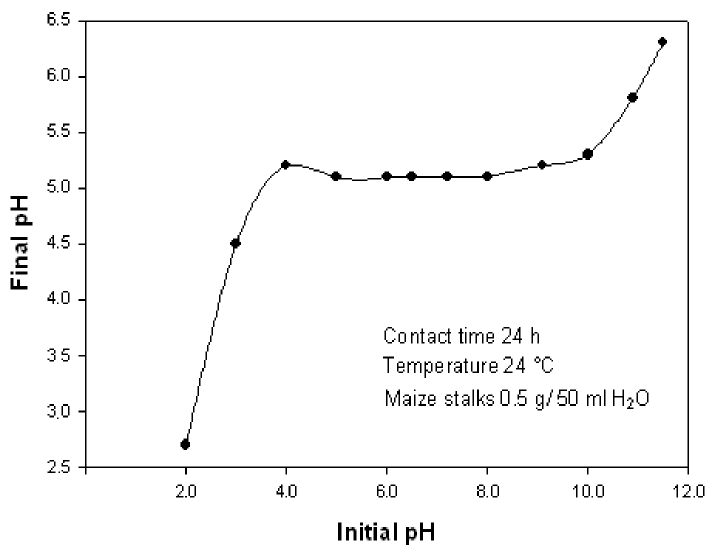

Figure 1: Point of zero charge (pHZPC) of maize stalks used for the adsorption experiments.

Batch sorption experiment

Using definite amount (0.5 g) of adsorbent in a 250 mL stopper conical flask containing 25 mL of metal ion solution, batch sorption studies were carried out at desired pH value, contact time, temperature and ionic strength.

Different initial concentration of Zn(II), Cd(II) or Mn(II) solutions were prepared by proper dilution from stock 1000 mg/L metal ions standard solutions. Standard metal ions solutions were prepared from the following salts: $Zn(NO_3)_2$, $Cd(NO_3)_2$ and $MnCl_2$. pH of the test solution was monitored by adding 0.1M HCl and 0.1M NaOH solution as required. The amount of biosorbent was then added to the metal ion solution in the conical flask and stirred for the desired contact time using a magnetic stirrer at 100 rpm. The time required for reaching equilibrium condition estimated by drawing samples at regular interval of time till the equilibrium was reached. The content of the metal ion in the test flask was separated from biosorbent by filtration through a filter paper and was analyzed by ICP-OES 2010 Serial Optical Emission Spectrometer, Optima (PerkinElmer). The samples were analyzed three times and the mean values were computed. The amount of metal ion adsorbed per unit mass of the biosorbent was evaluated by using following equations:

$$q_{max} = (C_0 - C_e)\frac{V}{W} \qquad (1)$$

Where, C_0 is the initial metal ion concentration, and C_e is the metal ion concentration at equilibrium and V is the volume of metal ion solution in milliliters, W is the mass of adsorbent in grams. The percent of metal ion removal was evaluated from the equation:

$$\%\,Removal = \frac{(C_0 - C_e)}{C_0} \times 100 \qquad (2)$$

Results and Discussion

Effect of pH on metal ion removal

The pH of the metal ion solution is an important parameter for adsorption of metal ions because it affects the solubility of the metal ions, concentration of the counter ions on the functional groups of the adsorbent and the degree of ionization of the adsorbate. To examine the effect of pH on metal ion removal efficiency, the pH was varied from 1.0 to 8.0 for Cd(II) and from 1.0 to 7.0 for Zn(II) and Mn(II) to prevent precipitation of metal hydroxides. As shown in Figure 2 the uptake of free ionic Cd(II) depends greatly on pH, where optimal metal removal efficiency occurs at pH 6.0 and then decreases at higher pH values, this behavior can be detected in other works [23]. Removal efficiency for Cd(II) increased from 7% to 46% over pH range from 1.0 to 6.0. In case of Zn(II), the metal uptake increases from 26% at pH 1.0 to 63% at pH 5.0, then it decreases by increasing the pH. The same figure indicated that the removal of Mn(II) increases from 16% at pH 1.0 to 38% at pH 7.0. This behavior is expected, as the acidity of the medium can affect the metal uptake on a biosorbent because hydrogen ions could compete with metallic ions for active sites on the biosorbent surface.

Effect of contact time and temperature

Figure 3 shows the effect of contact time on the rate of metal ion uptake onto maize stalks. At the beginning of adsorption, the values of % removal increased quickly, and then after 30 min, the change turned slow. Thus, the adsorption of the three metal ions on maize stalks was speedy. After about 90 min, the adsorbed quantity of the three metal ions showed nearly no change. The two stage sorption mechanism with the first rapid and quantitatively predominant and the second slower and quantitatively insignificant, has been extensively reported in literature [24,25]. This behavior gives away a slow approach to equilibrium. The nature of adsorbent and its available sorption sites affected the time needed to reach the equilibrium [26].

The effect of temperature of the adsorbate was also examined for solutions of 1000 mg/L metal ion and 20 g/L adsorbent at optimum pH values. Figure 4 shows the biosorption of Zn(II), Cd(II) and Mn(II) ions as a function of the temperature. The biosorption percentage decreased from 52 to 28% for Zn(II) ions, from 34 to 16% for Cd(II) ions and from 39 to 13% for Mn(II) ions as temperature was increased from 25 to 55 ºC for the equilibrium time 90 min. These results indicated the exothermic nature of Zn(II), Cd(II) and Mn(II) biosorption onto maize stalks. A decrease in metal ion biosorption with the rise in temperature may be due to either the damage of active binding sites in the biomass [27] or increasing tendency to metal desorption from the interface to the solution [28] by weakening of adsorptive forces between the active sites of the adsorbent species [29].

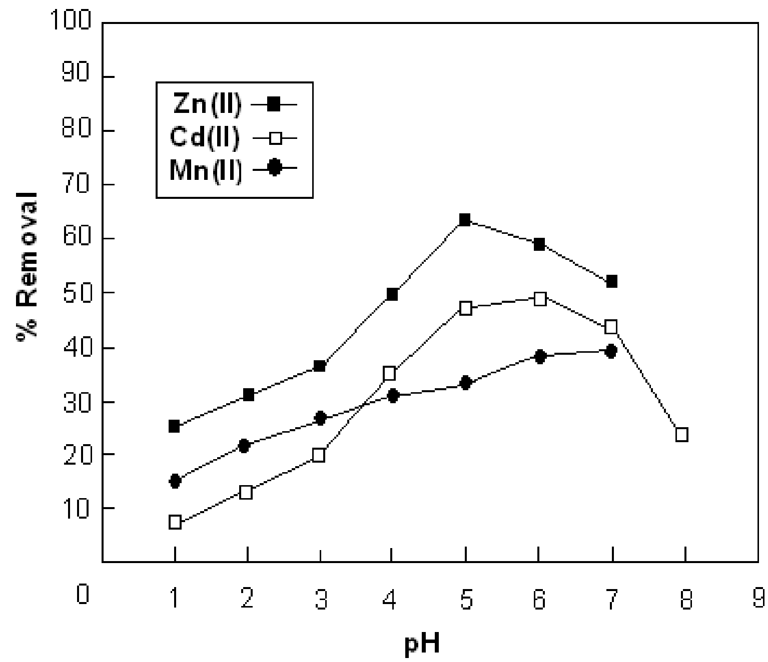

Figure 2: Effect of pH on the percent removal of Zn(II), Cd(II) and Mn(II) using maize stalks as adsorbent

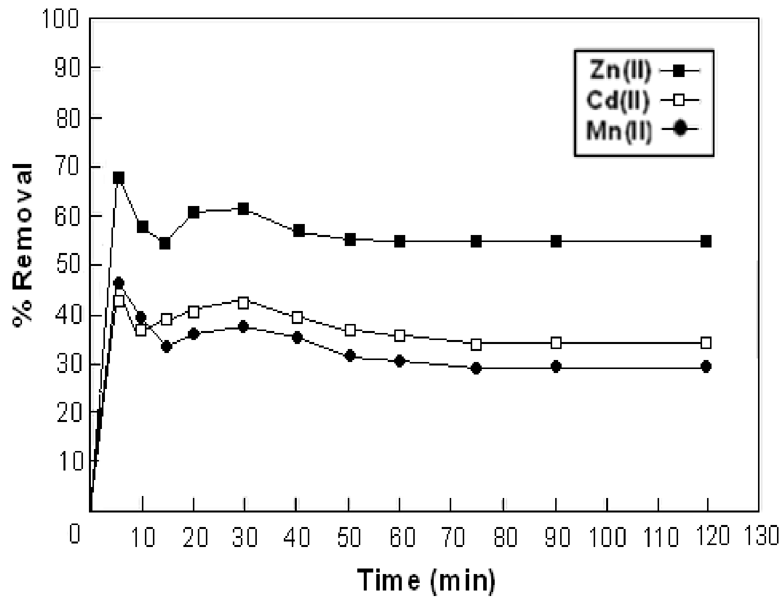

Figure 3: Effect of contact time on metal ion removal at optimum pH value

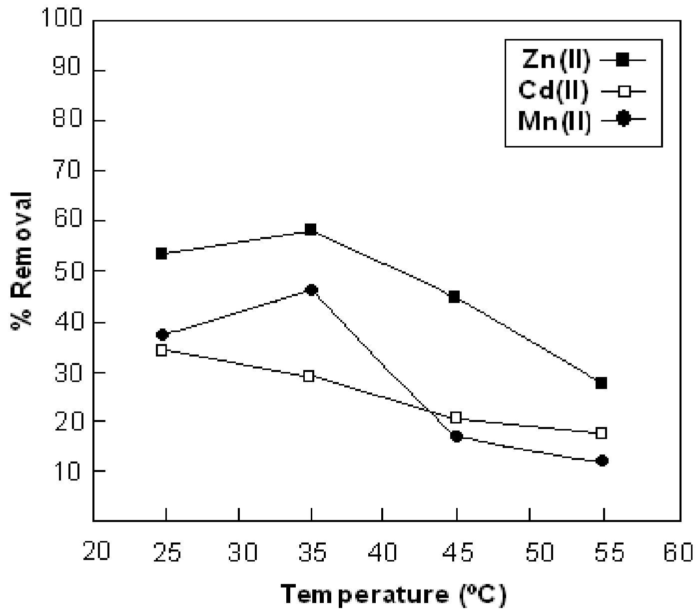

Figure 4: Effect of temperature on metal ion removal on maize stalks

Effect of ionic strength

The Influence of ionic strength I on heavy metal ions sorption by different biosorptions was investigated to determine solution chemistry effects. Different I values (0.1-1.0) were used by adding definite weights of solid KCl to a definite concentration of the metal ion (1000 mg/L). From the results obtained (Figure 5), it can be seen that the increasing of the ionic strength results in a decrease in the amount of the metal ion adsorbed as a result of the competition between the metal ions and the salt ions [30]. The reduction in uptake is probably due to the excess of K^+ ions which inhibit the approach of adsorbed ions to the active sites of the sorbent. Generally, there are two possible ways by which increasing I can influence metal ion sorption on different adsorbents: (1) decrease the solution-phase activity of metal ion and (2) increases concentration of competing ion (K^+). With increasing I, there is a little decrease in metal ion removal which can be attributed to the presence of sorption sites of different affinities.

Effect of initial metal ion concentration

The metal uptake mechanism is particularly dependent on the initial heavy metal concentration; at low concentrations, metal ions are adsorbed by specific active sites, while with increasing metal concentrations the binding sites become more quickly saturated as the amount of biomass concentration remained constant [31]. Figure 6 shows that the amount of metal ion sorbed per unit mass of maize stalks (i.e., sorption capacity) at optimum pH values and after 90 min of contact time was increased with the increase of the initial concentration of metal ion. It was observed also from the same figure that the adsorption capacity decreases in the following manner Zn(II) > Cd(II) > Mn(II). In the same time, the percentage removal was decreased with increasing the initial metal ion concentration for all metal ions studied.

Adsorption isotherms

To describe the adsorption process of Zn(II), Cd(II) and Mn(II) onto maize stalks, the three empirical models of Langmuir, Freundlich and Temkin isotherms were tested. The adsorption studies were conducted at fixed adsorbent dosage (0.5 g) by varying initial concentrations of heavy metals (40-1000 mg/L). These isotherms relate metal uptake per unit weight of adsorbent q_e to the equilibrium metal ion concentration in the bulk phase C_e.

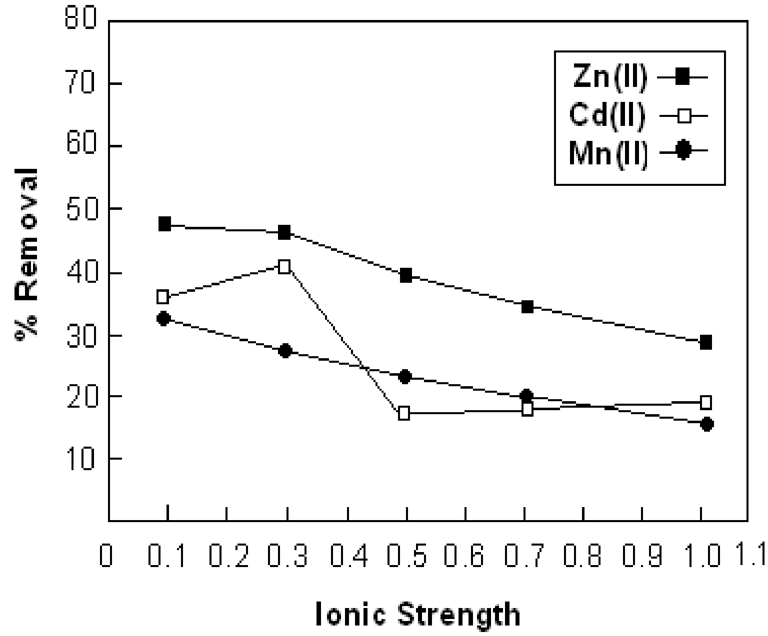

Figure 5: Effect of ionic strength on metal ion removal on maize stalks

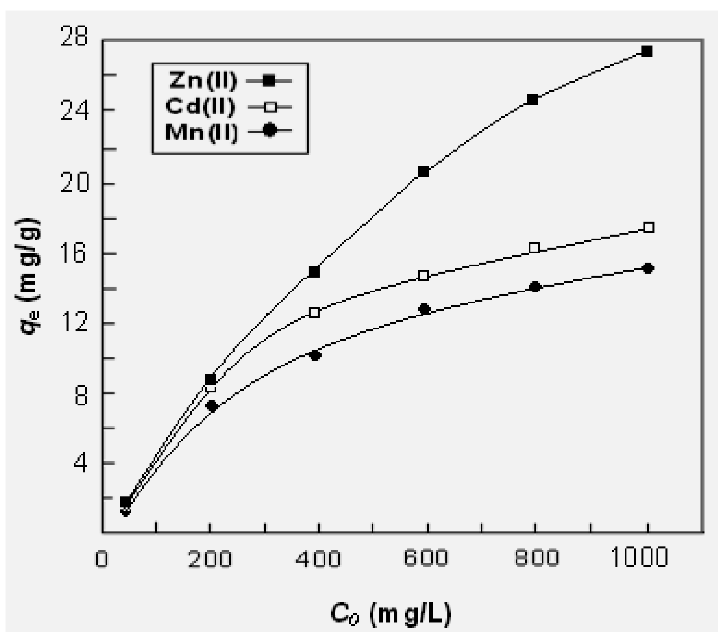

Figure 6: Effect of initial metal ion concentration on sorption capacity using maize stalks as adsorbent

The Langmuir Model

The Langmuir isotherm models is used to describe the relationship between the amount of adsorbed material and its equilibrium concentration in solutions. The Langmuir isotherm is valid for monolayer adsorption on a surface containing finite number of identical sites. The model assumes a uniform adsorption on the surface and transmigration in the plane of the surface. The Langmuir isotherm is expressed as follows [32]:

$$q_e = (K_L C_e)/(1 + bC_e) \qquad (3)$$

where, q_e is the adsorption capacity at equilibrium in mg/g, C_e is the concentration at equilibrium (mg/L) and K_L is the Langmuir equilibrium constant in (mL/mg) and is expressed as follows:

$$K_L = Q_0 b \qquad (4)$$

where, Q_o is the adsorption capacity at saturation in mg/g and b the adsorption coefficient in L/mg; The linear form of Langmuir isotherm model can be represented by using the equation below:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \qquad (5)$$

The linear plots of Ce/q_e vs C_e show that adsorption follows the Langmuir adsorption model (Figure 7). The values of Q_o and b can be calculated (Table 1) from the slope and intercept of the plot, respectively. The correlation coefficients are 0.932, 0.998 and 0.989 for Zn(II), Cd(II) and Mn(II), respectively. These results reveal that the Langmuir-type sorption isotherm is suitable for equilibrium studies For Cd(II) and Mn(II) only, suggesting the formation of monolayer coverage of the adsorbate on the surface of adsorbent for these metalions [33]. The amount of metal ions adsorbed per unit mass of the adsorbent increased with the metal concentration as expected and the sorption capacities were 30.30, 18.05 and 16.61 for Zn(II), Cd(II) and Mn(II) ions, respectively.

The essential characteristics of the Langmuir isotherm can be explained by the equilibrium separation factor R_L defined as follows:

$$R_L = 1/(1 + bC_0) \qquad (6)$$

Depending on the value of R_L, the shape of the isotherm and whether the adsorption is favorable or not can be determined. The calculated R_L values for Zn(II), Cd(II) and Mn(II) at 298 K, were represented in Table 1. It was observed that at these experimental conditions, sorption of the different metal ions by maize stalks was found to be a favorable process [34] as the values of R_L are 0.719, 0.895 and 0.905 for Zn(II), Cd(II) and Mn(II), respectively.

The maximum adsorption capacities (Q_0) of adsorbent calculated from Langmuir isotherm equation which defines the maximum capacity of the adsorbent for metal ions were found to be comparable with other adsorbents reported in the literature for Zn(II), Cd(II) and Mn(II), Table 1.

The Freundlich Model

The Freundlich isotherm assuming that the adsorption process takes place on heterogeneous surfaces and adsorption capacity is related to the concentration of the adsorbent. The Freundlich model is based on the following expression [51]:

$$q_e = K_F C_e^{1/n} \qquad (7)$$

where, K_F is the Freundlich constant and $1/n$ is a constant indicating the reaction intensity. The two Freundlich parameters K_F and $1/n$ can be determined graphically by plotting the experimental data and then using the Freundlich equation in the following form:

$$ln\, q_e = ln\, K_F + (1/n) lnC_e \qquad (8)$$

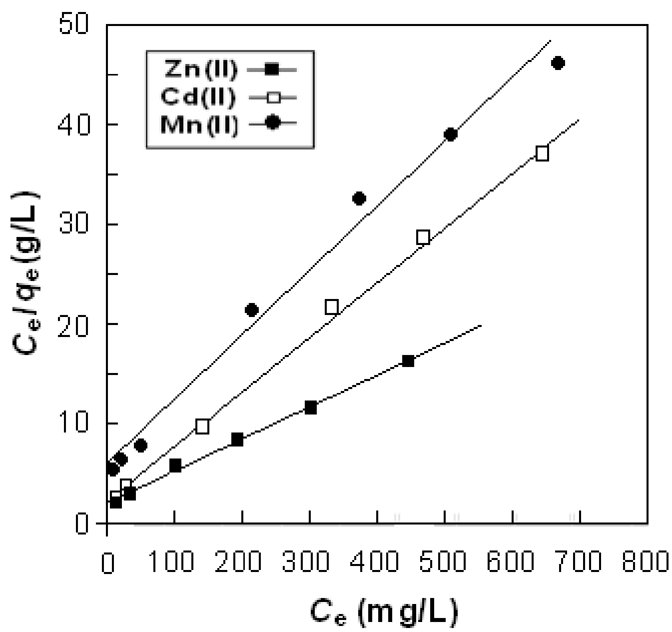

Figure 7: Langmuir isotherm plot for the adsorption of Zn(II), Cd(II) and Mn(II) on maize stalks at optimum pH values.

Table 1: Langmuir constant for different adsorbents

Metal	Adsorbent	Langmuir constant, Q_0 (mg/g)	Reference
Zn(II)	Sunflower stalks	30.7	35
	Black Locust	5.0	36
	Oak saw dust	6.9	36
	Carrot residues	29.6	37
	Saw dust	14.1	29
	Neem bark	13.3	29
	Sugar beat pulp	17.7	38
Cd(II)	Groundnut husk	42.7	39
	Sugar cane bagasse	149.9	40
	Olive cake	65.4	41
	Lignite	40.2	42
	Spent grain	17.3	43
	Maize bran	7.4	44
	Tree fern	16.3	45
Mn(II)	*Pseudomonas aeruginosa*	22.4	46
	natural zeolitic tuff	10.0	47
	chitin	0.643	48
	kaolinite	0.446	49
	Cyanobacterium *Gloeothece Magna*	0.473-0.906	50

The variations of ln q_e with ln C_e for zinc, cadmium and manganese cations are shown in Figure 8. It can be seen from the linear relationship that the adsorption of the three metals on maize stalks follows the Langmuir model. The values of K_F and n are presented in Table 1. The n values are 2.01, 2.48 and 2.23 for Zn(II), Cd(II) and Mn(II), respectively (greater than 1), indicating that the adsorption is favorable [52].

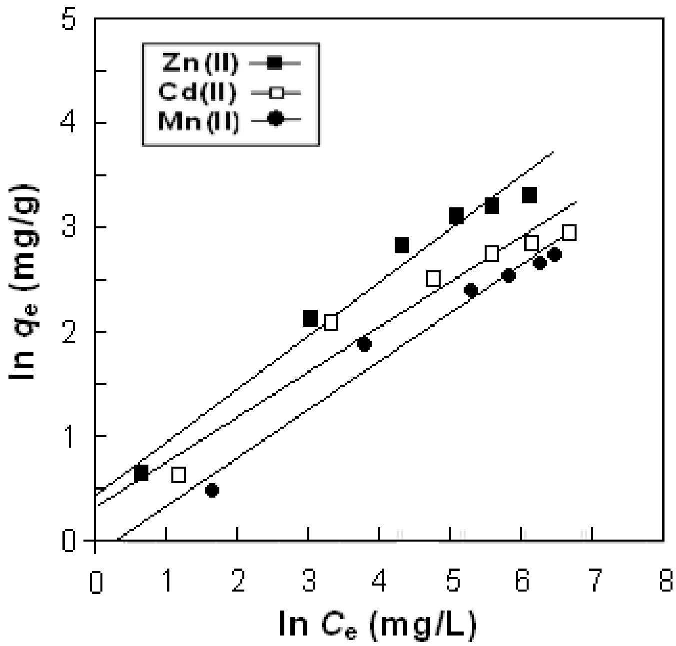

Figure 8. Freundlich isotherm plot of Zn(II), Cd(II) and Mn(II) on maize stalks

It can be observed from the correlation coefficient values (R^2) in Table 2 that Freundlich isotherm model exhibited good fit to the sorption data of Zn(II) and Mn(II).

The Temkin Isotherm

This isotherm was developed by Temkin and Pyzhev [53], and it is based on the assumption that the heat of adsorption decreases linearly with the increase of coverage of adsorbent [54]. Temkin isotherm assumes that the fall in the heat of sorption is linear rather than logarithmic [55]. This model can be shown by the equation:

$$q_e = \frac{RT}{b_T} lnK_T + \frac{RT}{b_T} lnC_e \quad (9)$$

where, K_T (L/g) is Temkin adsorption potential and b_T (kJ/mol) is heat of sorption (Table 1). The linear plot of ln C_e versus q_e for the three metal ions for Temkin model is shown in Figure 9. From the slope and intercept of the straight line b_T and K_T can be evaluated, respectively.

Table 2: Modeled Langmuir and Freundlich isotherms parameters for zinc(II), cadmium(II) and manganese(II) adsorption on maize stalks

Metal Ion	Lagmuir Isotherm				Freundlich Isotherm			Temkin Isotherm		
	Q_0 (mg/g)	b (L/mg)	R_L (L/mg)	R^2	K_F ($L^n mg^{1-n}/g$)	n	R^2	K_T (L/g)	b_T (kJ/mol)	R^2
Zn(II)	30.30	0.017	0.268	0.932	1.517	2.01	0.983	0.47	515.1	0.944
Cd(II)	18.05	0.023	0.213	0.998	1.509	2.48	0.925	0.64	866.3	0.994
Mn(II)	16.61	0.009	0.410	0.989	0.842	2.23	0.975	0.64	945.6	0.957

By comparing the correlation coefficients (R^2) obtained from the three isotherms plots plots (Table 1), it can be concluded that Langmuir model can be applied successfully to Cd(II) and Mn(II) and Freundlich model can be applied to Zn(II) and Mn(II), while Temkin isotherm model appears to be favorable for fitness to the experimental data of Cd(II).

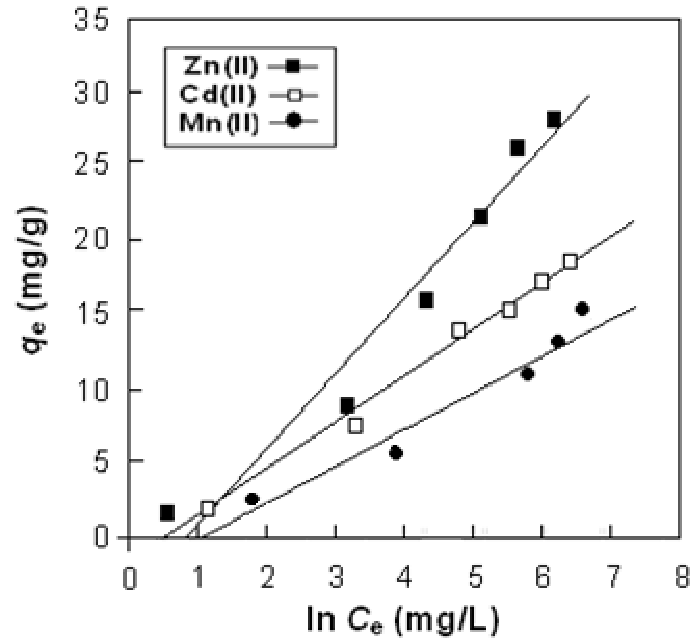

Figure 9. Temkin isotherm plot of Zn(II), Cd(II) and Mn(II) on maize stalks

Thermodynamic Parameters

The temperature dependence of the thermodynamic parameters on the adsorption of Zn(II), Cd(II) and Mn(II) on maize stalks were calculated using equations [56]:

$$\Delta G^o = -RT\ ln\ K \qquad (10)$$

The Gibbs free energy change (ΔG^o) is related to the entropy change (ΔH^o) and enthalpy change (ΔS^o) at constant temperature by the following equation:

$$\Delta G^o = \Delta H^o - T\Delta S^o \qquad (11)$$

Combining the above two equations, we get:

$$\ln K = -\frac{\Delta H^o}{RT} + \frac{\Delta S^o}{R} \qquad (12)$$

where, R is the universal gas constant (8.314 J/mol K), T is the absolute temperature (K) and K is the Langmuir equilibrium constant. ΔG^o was calculated at different temperatures from equation (9). By plotting the values of ln K versus 1/T (Figure 10) using equation (11), the values of ΔH^o and the ΔS^o were calculated from the slope and intercept, respectively, Table 3.

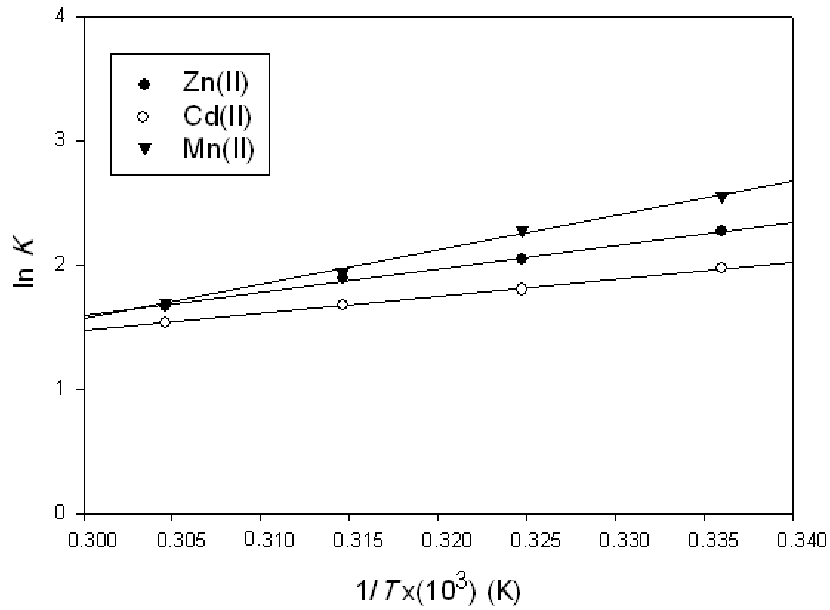

Figure 10. Plot of ln K vs. 1/T for removal of Zn(II), Cd(II) and Mn(II) by maize stalks

Table 3: Thermodynamic parameters of Zn(II), Cd(II) and Mn(II) on maize stalks at initial metal ion concentration 1000 mg/L

Metal ion	*T* (K)	ΔG^o (KJ/mol)	ΔH^o (KJ/mol)	ΔS^o (J/mol K)
Zn(II)	298	-3.244	-24.27	-10.97
	308	-3.354		
	318	-3.464		
	328	-3.573		
Cd(II)	298	-3.800	-14.17	-12.80
	308	-3.928		
	318	-4.056		
	328	-4.184		
Mn(II)	298	-7.406	-25.35	-24.94
	308	-7.656		
	318	-7.905		
	328	-8.155		

The negative values of Gibbs free energy change (ΔG^o) indicate that the adsorption process for the three metal ion7s is feasible and spontaneous. It was observed that the values become more negative with increase in temperature. The negative values of ΔH^o indicate that the adsorption of metal ions on maize stalks is exothermic. The negative values of ΔS^o suggest decreased randomness at the solid/solution interface and no significant changes occur in the internal structure of the adsorbent through the adsorption of metal ions onto maize stalks [57].

Conclusion

The biosorption of Zn(II), Cd(II) and Mn(II) on maize stalks was investigated. Adsorption of the three metal ions is dependent on their initial concentrations and pH of the metal solution and the equilibrium were attained after 90 min of mixing. The results indicate that the optimum pH for maximum removal of Zn(II), Cd(II) and Mn(II) ions are 7.0, 6.0 and 5.0, respectively. The adsorption process was found to be exothermic. Langmuir adsorption model can be applied successfully with cadmium and manganese, Freundlich adsorption model fitted well with zinc and manganese, while Temkin model can be applied to cadmium. The sorption capacities were 30.03, 18.05 and 16.61 mg/g for Zn(II),Cd(II) and Mn(II) ions, respectively. Maize stalks which is an agricultural waste material can be used for industrial water treatment to eliminate low concentrations of heavy metal ions as zinc, cadmium and manganese.

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