Chemsearch Journal 3(1): 7 – 12 June, 2012
Publication of Chemical Society of Nigeria, Kano Chapter
Date Received: December, 2011
Date Accepted: February, 2012
ISSN: 2276 – 707X

THERMODYNAMICS AND ADSORPTION ISOTHERMS FOR THE BIOSORPTION OF Cr(VI), Ni(II) AND Cd(II) ONTO MAIZE COB

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ABSTRACT

The use of maize (Zea mays) cob for the biosorption of Cr(VI), Ni(II) and Cd(II) is reported. Biosorption experiments were carried out using batch process with 8g weight of adsorbent and variable adsorbate concentrations. Variations in the concentration of the different adsorbates during the adsorption process were monitored by the use of Shimadzu AA650 Double Beam Atomic Absorption/Flame spectrophotometer. Thermodynamic quantities such as ΔH and ΔS were determined in which ΔH varied from 1,271.21Jmol^{-1} to 1,466.59Jmol^{-1} at 20mg/L adsorbate concentration and 1,276.20 to 1,872.42Jmol^{-1} at 60mg/L suggesting increasing endothermicity of the adsorption process. The adsorption process was found to be spontaneous, with spontaneity increasing with increase in adsorbate concentration and temperature. Also, the ΔG values suggested high affinity of Cr over the other adsorbates. Equilibrium data were tested using Freundlich and Langmuir adsorption isotherms. The values of the numeric constants n and K_F from Freundlich plots and the linearity of their plots suggested a chemisorption process closely defined by Freundlich isotherm.

Keywords: Adsorbate, Adsorbent, Adsorption isotherms, Maize cob, Thermodynamics

INTRODUCTION

Maize (*Zea mays*) cob was selected for this study because of its relative abundance in Nigeria. Maize is a major staple cereal in Nigeria and, therefore, produces large volume of waste. Maize is widely believed to have the greatest potential among food crops for attaining the technological breakthroughs that will improve food production (Smith *et al*., 1997). Almost all the different uses of maize disposed-off the cobs and this constitutes waste problems. The cobs were therefore tested in this work as potential adsorbents for metallic ion removal from wastewater particularly since conventional methods are expensive. Therefore, the need to develop cheaper methods in a developing country like Nigeria becomes imperative.

Most of the reported work on the use of agricultural by-products for removal of heavy metals has to do with the capability of such materials in adsorbing heavy metals (Quek *et al.*, 1998). The principle behind exploring agricultural by-products in this work is the fact that most agricultural by-products are composed of cellulose in the plant cell walls.

As reported by Abdel-Ghani *et al*. (2007), infrared spectrum of maize cobs shows two strong bands at 3479.3 and 3413.8cm^{-1} which were attributed to stretch (N-H) of amide. The medium band at 3556.5 cm^{-1} and that at 2920 cm^{-1} assume the existence of H-bridges and some crystal water. The strong band observed at 1041.5 cm^{-1} indicates the stretching of the many C-OH and C-O-C bonds.

The use of maize cob as granular or powdered, for the removal of metals such as lead, cadmium, zinc and mercury both from aqueous solution and industrial effluent and the studies of the kinetics and intraparticulate diffusivities of the adsorption process have been reported by workers such as Opeaolu *et al*. (2009), Abia and Igwe (2005) and Jignesh and Padmaja (2008). In all cases the substrate has been promising, and this lead to its choice for this work.

The work of Igwe and Abia (2007) on the effect of temperature and particle size on bioremediation of As(III) from aqueous solution using modified and unmodified coconut fiber reported ΔG values which are less than -15kJmol^{-1} indicating a spontaneous and physical adsorption process, with the modified fiber showing higher remediation of the adsorbate.

METHODOLOGY

Materials

All glasswares and plastic containers were washed with detergents, rinsed with distilled water and then soaked in a 10% HNO_3 solution for 24hrs. They were then washed with deionised water and dried in an oven for 24hrs at 80°C (Todorovi *et al*., 2001).

Distilled-deionised water and AnalaR grade reagents were employed for the preparation of all stock solutions. 1000mg/L of Cr(VI), Ni(II) and Cd(II) were respectively prepared by dissolving 2.8290g of $K_2Cr_2O_7$, 4.0503g of $NiCl_2.6H_2O$ and 2.1930g of $CdSO_4.8/3H_2O$ in small volumes of distilled deionised water in separate beakers and the solutions were transferred to a 1.0litre volumetric flasks followed by the addition of 100cm^3 of 6M HNO_3 and they were made to mark with more water (Svehla, 2006). Lower working concentrations were prepared daily from the stock solution by appropriate dilution.

Maize (*Zea mays*) cob (MC) adsorbent was collected from local farm in Minjibir, Kano state, Nigeria. They were cut into small pieces, washed several times with water, air – dried and ground to 850µm particle size and finally kept in plastic containers for subsequent use.

Methods

Batch adsorption experiments in which the same solution remains in contact with a given quantity of adsorbent till equilibrium between the adsorbate concentration in solution, and the adsorbate adsorbed per unit weight of adsorbent, is reached was employed in this work. This type of equilibrium established is static in character, as it does not change further with time. A harmonised procedure as described by Bhattacharya *et al*. (2008) and El-Nemr *et al*. (2008) for testing the adsorption properties of the adsorbent was followed at 303K, and repeated at 313K, 323K and 333K temperatures. The details of the procedure involve shaking 8g of the adsorbent with a known volume of the adsorbate (100 cm^3) in a screw capped Erlenmeyer flasks having initial loading concentrations ranging from 20–60 mg/L on an Innova 4000 mechanical shaker from New Brunswick Scientific at a speed of 290 rpm for a equilibrium period of 1.00 hr. The pH of the adsorbate solutions were adjusted with help of 0.5 M HCl and 0.5 M NaOH solutions. After all agitations each sample was filtered using Whatman No. 1 filter paper. Residual adsorbate concentrations were determined using Shimadzu AA650 double beam atomic absorption/flame spectrophotometer. Blank solution prepared by diluting 10 cm^3 of 6M HNO_3 solution to mark in a 100 cm^3 standard volumetric flask was used to flush the spectrophotometer by aspirating between the standard and sample measurements.

RESULTS AND DISCUSSION

Adsorption Thermodynamics

Adsorption processes are common examples of heterogeneous equilibria in which an adsorbate in the form of a gas molecule or an aqueous solution (M^{n+}) is attached to some favourable sites of a given substrate ($S_{(s)}$) which most often is a solid material such that:

$$M^{n+}_{(aq)} + S_{(s)} \rightleftharpoons S - M_{(ad)}$$

Adequate knowledge of the thermodynamic quantities for the equilibrium process allows for the proper understanding of the spontaneity and changes in energy during the entire sorption process. Parameters such as K_a, ΔH, ΔS and ΔG were obtained from the changes of the adsorbate concentration during the sorption process using relevant thermodynamic relations as highlighted elsewhere (Chen and Wang, 2006; Omar and Al-Itawi, 2007; Zawani *et al*., 2009; Ibrahim, 2011; Ibrahim and Jimoh, 2011) and were tabulated in Tables 1 and 2, respectively. It is evident that the values of ΔH_{ad} were positive, i.e. endothermic, with endothermicity increasing at higher adsorbate concentration. One possible interpretation of endothermicity of the adsorption was that the metal ions were highly solvated in water. In order for these ions to be adsorbed, the hydration sphere must be removed, and this process requires energy intake. This energy of dehydration supersedes that required for getting the ions attached to the surface of the adsorbent (Chen and Wang, 2006).

Also evident from the tables is the positive nature of the ΔS_{ad} values, suggesting spontaneous process. This occurs as a result of redistribution of energy between the adsorbate and the adsorbent. Before adsorption occurs, the metallic ions near the surface of the adsorbent were more ordered than in the subsequent adsorbed state. This increase in randomness at the solid – solution interface during the adsorption process leads to the increase in entropy and hence an overall positive ΔS. The adsorption process is therefore likely to occur spontaneously at both normal and at high temperatures as indicated from the calculated ΔG_{ad} values (Hefne e*t al*., 2008; Vasu, 2008; Andal and Sakthi, 2010).

The Gibbs free energy change (ΔG_{ad}) was negative as expected for a spontaneous process under the applied conditions. The decrease in ΔG_{ad} (i.e. increase negative) values with increase in temperature indicated more efficient adsorption at higher temperature. This is because at higher temperatures ions are easily desolvated and therefore their adsorption becomes more favourable (Qadeer, 2005; Chen and Wang, 2006; Hefne e*t al*., 2008). The result also revealed that at the highest temperature (333K) and higher adsorbate concentration (60mg/L), the adsorption of Cr ion was the most spontaneous (ΔG_{ad} = -10,600.70$Jmol^{-1}$) while that of Cd was the least spontaneous, ΔG_{ad} = -5,401.57$Jmol^{-1}$.

Adsorption Isotherms

Adsorption isotherm studies were carried out with a fixed initial adsorbent dose (8g) and varying adsorbate concentrations (Baral *et al*., 2006) and the applicability of the data were tested for the Freundlich adsorption isotherm represented as:

$$\ln q_e = \ln K_F + a \ln C_e.$$

and Langmuir (Type 1) adsorption isotherm represented as:

$$\frac{C_e}{q_e} = \frac{1}{kq_m} + \frac{C_e}{q_m}$$

Freundlich isotherm gives an expression encompassing the surface heterogeneity and the exponential distribution of active sites and their energies. Fig. 1 gives the Freundlich plots of the various adsorption data for the metal ions onto the maize cob adsorbent. The numerical values of the constants n_F and K_F for the plots in Fig.1 were determined from the slopes and intercepts of the respective plots and are presented in Table 3. The constant K_F is indicative of the relative adsorption capacity of the adsorbent related to the bonding energy and can be defined as the adsorption or distribution coefficient. It represents the quantity of the metal ion adsorbed onto the adsorbent for unit equilibrium concentration.

The constant $a = 1/n_F$, where n_F is the heterogeneity factor, represents the deviation from linearity of adsorption as follows: if the value of $n_F = 1$, the adsorption is linear; if $n_F < 1$, the adsorption process is chemical, and if $n_F > 1$, the adsorption is a favourable physical process (Crini *et al*., 2007). Also for all values of $1/n_F$ less than unity, adsorption is the predominant process taking place otherwise desorption becomes predominant.

The observed value of $n_F < 1$ for the adsorption of the three adsorbates and the linearity of their plots are indicative of the fact that the result of the experimental data for the adsorption of these metals fitted well to the Freundlich isotherm as a typical chemisorptions process. In an earlier work (Ibrahim, 2011) the adsorption of the same metal ions onto sawdust with the exception of Cd were found to fit the Freundlich isotherm.

The Langmuir model represents one of the first theoretical treatments of non-linear sorption and suggests that the uptake occurs on a homogeneous surface by monolayer sorption without interaction between the adsorbed molecules (Bansal *et al*., 2009). The constants k and q_m for Langmuir isotherm are the adsorption equilibrium constant (dm^3/mg) and monolayer adsorption capacity of the adsorbent (mg/g), respectively. The values of these constants were also computed from the slopes and intercepts of the Langmuir plots (Fig. 2) and are presented in Table 3. The negative nature of the values for the adsorption equilibrium constant (k) for the adsorption of all the adsorbates onto the adsorbent may be linked to the observation that the adsorption of these metal ions does not fit the Langmuir model. Hence also leading to the low values for the monolayer coverage (q_m).

A feature that is an essential character of the Langmuir isotherm is the dimensionless separation parameter R_L, which is indicative of the isotherm shape that predicts whether an adsorption system is favourable or unfavourable. R_L according to Malik (2004), Ibrahim *et al*. (2006) and Nwabanne and Igbokwe (2008) is calculated using the relation:

$$R_L = \frac{1}{1 + kC_o}$$

where C_o is the initial metal ion concentration(mg/L) and k is adsorption equilibrium constant obtained from the intercept of the Langmuir plot. The value of R_L indicates the type of the isotherm to be either (i) unfavourable (chemisorption is the predominant process) if $R_L > 1$, (ii) linear (both chemisorption and physisorption are taking place nearly at the same rate) if $R_L = 1$, (iii) favourable (physisorption is the predominant process) if $0 < R_L < 1$ or (iv) irreversible (non reversible chemisorptions process) if $R_L = 0$. The calculated values of the R_L for the different ions onto the maize cob adsorbent (Table 4) under the different conditions studied were all negative, a condition indicating that the adsorptions process does not fit to the Langmuir model.

Conclusion

The adsorption of the different ions studied was found to be thermodynamically spontaneous and feasible, with spontaneity increasing with increase in both ionic strength and temperature. The adsorption was also found to be chemical in nature as defined by the Freundlich adsorption isotherms.

Table 1: Thermodynamic Parameters for the Adsorption of the various Metal ions onto Maize Cob

	K_a	$\Delta G_{ad} = \Delta H_{ad} - T\Delta S_{ad}$ (Jmol^{-1})				ΔH_{ad} (Jmol^{-1})	ΔS_{ad} (Jmol^{-1}K^{-1})
		303K	313K	323K	333K		
Cr	0.0118	-3861.4	-4037.24	-4213.08	-4388.92	1466.5896	17.5841
Ni	0.0062	-1167.32	-1247.80	-1328.28	-1408.76	1271.2106	8.0480
Cd	0.0143	-2977.67	-3120.42	-3263.17	-3405.92	1347.6994	14.2751

Conditions: 8g Adsorbent, 20mg/L metal ion concentration and 1hr Agitation time

Table 2: Thermodynamic Parameters for the Adsorption of the various Metal ions onto Maize Cob

	K_a	$\Delta G_{ad} = \Delta H_{ad} - T\Delta S_{ad}$ (Jmol^{-1})				ΔH_{ad} (Jmol^{-1})	ΔS_{ad} (Jmol^{-1}K^{-1})
		303K	313K	323K	333K		
Cr	0.0273	-9481.01	-9854.23	-10227.40	-10600.70	1,872.4172	37.3215
Ni	0.0238	-7075.70	-7362.79	-7649.87	-7936.95	1,622.8928	28.7082
Cd	0.0425	-4799.97	-5000.51	-5201.04	-5401.57	1,276.1990	20.0534

Conditions: 8g Adsorbent, 60mg/L metal ion concentration and 1hr Agitation time

Table 3: Numeric Constants for the Adsorption of the Metal ions onto the Adsorbents

Ion	Freundlich		Langmuir	
	n_F	K_F	q_m (mg/g)	k (L/mg)
Cr	0.2967	2.669×10^{-5}	500	-0.0769
Ni	0.2319	1.0520×10^{-6}	500	-0.0541
Cd	0.1872	4.6026×10^{-7}	100	-0.1020

Table 4: Variation of R_L for the Adsorption of the Various Adsorbates onto Maize Cob with Increase in Initial Metal Ion Concentration

Co (mg/L)	R_L Cr	Ni	Cd
20	-1.8571	-12.333	-0.9608
30	-0.7647	-1.6087	-0.4852
40	-0.4815	-0.8605	-0.3245
50	-0.3514	-0.5873	-0.2438
60	-0.2766	-0.4458	-0.1952

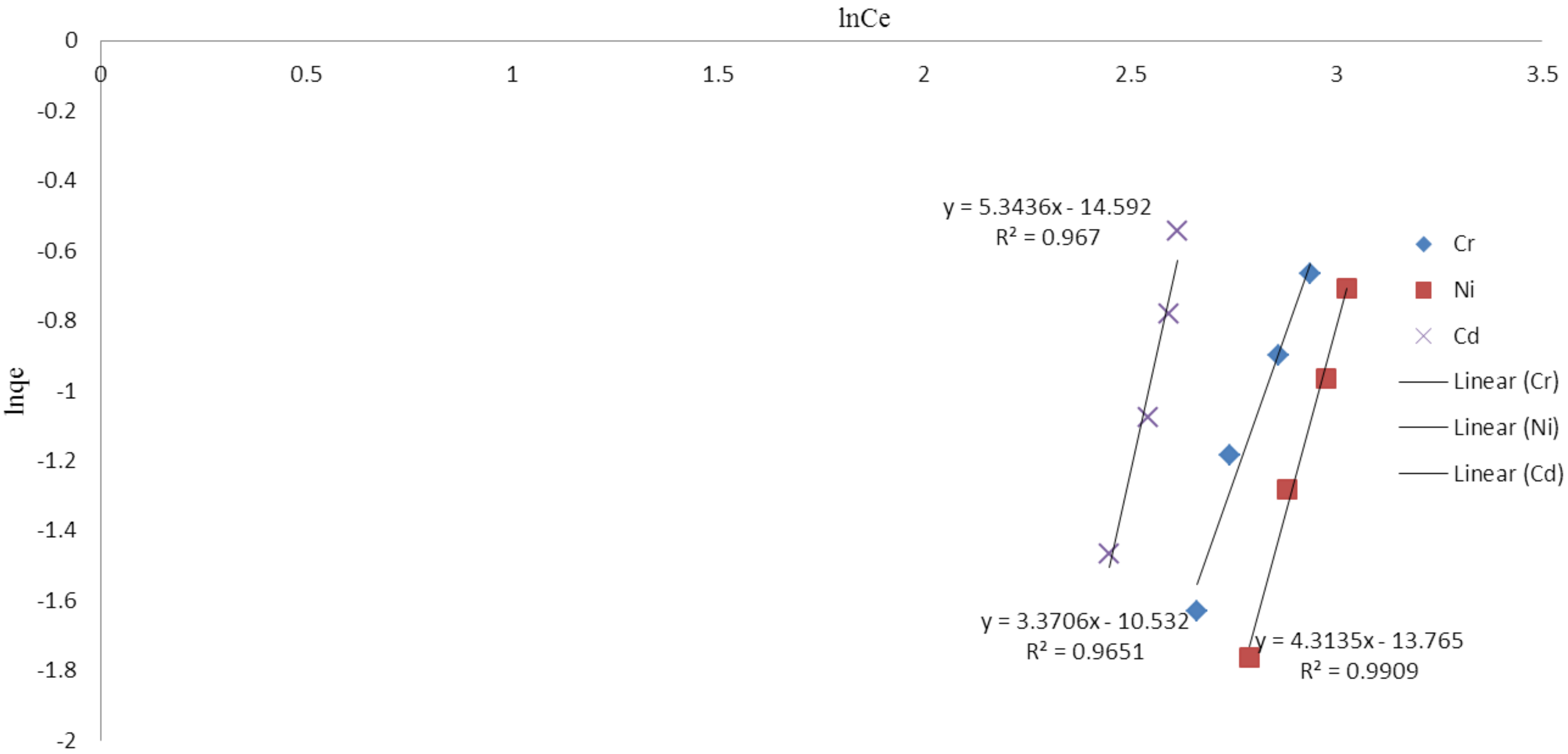

Fig. 1: Freundlich Adsorption Isotherm for the Adsorption of the Metal Ions onto Maize Cob for 1hr Agitation

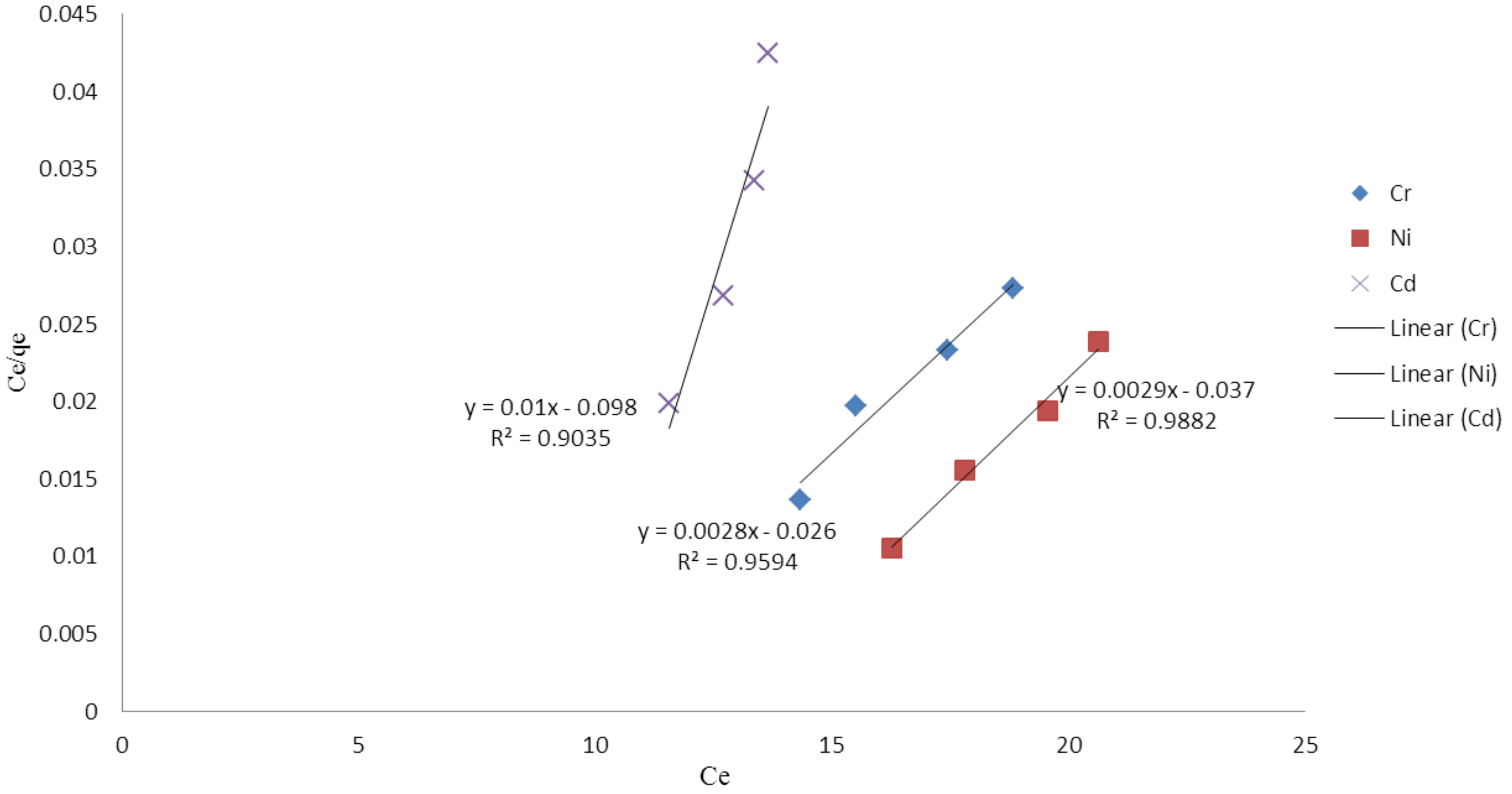

Fig. 2: Langmuir Adsorption Isotherm for the Adsorption of the Metal Ions onto Maize Cob for 1hr Agitation

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