

Thermodynamics and Adsorption Efficiencies of Maize Cob and Sawdust for the Remediation of Toxic Metals from Wastewater

Muhammad B. Ibrahim

Department of Pure and Industrial Chemistry, Bayero University, Kano, Nigeria
Email: mbibrahim.chm@buk.edu.ng

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The thermodynamics and sorption efficiencies for the remediation of Cr, Ni and Cd from their aqueous solutions using Maize Cob (MC) and Sawdust (SD) in a batch system are reported. Efficiencies were judged based on parameters such as sorbent weight, initial adsorbate loading concentration, pH and surface area. Shimadzu AA650 Double Beam Atomic Absorption/Flame spectrophotometer was employed to study concentration differences before and after the adsorption process. Parameters such as ΔH , ΔS and ΔG were determined. On MC, ΔH varied as 1466.59, 1271.21 and 1347.70 kJmol⁻¹ for Cr, Ni and Cd respectively. While on SD it varied as -566.85, 256.32 and 888.77 kJmol⁻¹ respectively for the same order of metal ions. The three ions were found to be chemisorbed onto MC, while on SD Cr and Ni were physisorbed and Cd remains chemisorbed as suggested by Freundlich isotherm.

Keywords: Adsorbate; Adsorbent; Maize Cob; % Removal; Sawdust; Wastewater

Introduction

Unlike organic pollutants which are biodegradable, heavy metals like Cr(VI), Ni(II), Cd(II) etc. are not biodegradable; and their increasing concentration in the environment is detrimental to a variety of living species. Excessive ingestion of these metals by humans can cause accumulative poisoning, cancer, nervous system damage and ultimately death. This forms the basis for the increasing researches with a view to remedying their levels in the environment; and also the growing concern by governmental agencies for the regulation of the discharge of these metals into the environment. Different methods for the removal of toxic metals from aqueous systems have been reported by different workers amongst which adsorption onto natural adsorbents have proven to be an efficient and inexpensive option for removal of heavy metals from wastewater (Rafika et al., 2009; Kehinde et al., 2009; Khan et al., 2004). Maize cob is mainly composed of lingocellulose materials having relatively large surface areas that can provide intrinsic adsorptive sites to many substrates and inherently adsorb waste chemicals such as dyes and cations in water due to columbic interaction and physical adsorption (Sun & Shi, 1998). According to Shukla et al. (2002) the cell walls of sawdust mainly consist of cellulose and lignin, and many hydroxyl groups, such as tannins or other phenolic compounds which are all active ion exchange compounds. Lignin, the third major component of the wood cell wall, is a polymer material, which is built up from the phenyl-propane nucleus, i.e. an aromatic ring with a three-carbon side chain.

Materials and Methods

The water used throughout this work was initially distilled and then passed through a deionizer. Analar grade reagents were employed for the preparation of all stock solutions and refrigerated. Fresh working standards were prepared daily by

appropriate dilution of the stock solutions. All glassware and plastic containers were washed with detergents, rinsed with distilled water and then soaked in a 10% HNO₃ solution for 24 h. They were then washed with deionised water and dried in an oven for 24 h at 80°C (Todorovi et al., 2001). The adsorbent employed in this work were maize cob and sawdust. Maize cobs (MC) collected from local farm were cut into small pieces, washed several times with water and air-dried. Similarly, hardwood sawdust (SD) of Mahogany (*Khaya senegalensis*) tree collected from a local saw mill was air-dried in sunlight until almost all the moisture evaporated. Then it was washed several times with distilled water in order to remove the water soluble tannins, after which it was dried in air and then in an oven at 80°C. The two substrates were then ground to two particle sizes (850 µm and powdered form) and were finally kept in plastic containers for subsequent use.

All batch sorption analyses were carried out at room temperature (30°C ± 2°C) by shaking various amounts of the adsorbents (2 - 8 g) with 100 cm³ of the aqueous solutions of the adsorbates (in a screw capped Erlenmeyer flasks) with initial loading concentrations ranging from 20 - 60 mg/L on an Innova 4000 shaker from New Brunswick Scientific at a speed of 290 rpm for a period of 1 h. Immediately after which, the samples were separately filtered using Whatman No. 1 filter paper and the filtrates collected in polyethylene bottles were taken for AAS measurements for the residual adsorbate concentration using Shimadzu AA650 double beam atomic absorption/flame spectrophotometer. All assays were replicated and only mean values are presented. pH adjustments of the adsorbate solutions were achieved by using .5 M HCl and .5 M NaOH solutions as required.

Results and Discussion

The affinities of the two substrates to the three adsorbates show a gradual increase from the lowest amount (2 g) to the

highest (8 g) as shown in **Figure 1**, a trend which can be attributed to the increase in surface active sites as the adsorbent dose is increased (Zhou et al., 2011). Similarly, from the figure sawdust shows higher affinity for the adsorbates, but Cd, compared to maize cob due to, among other factors, that it contains various organic compounds (lignin, cellulose and hemicellulose) with polyphenolic groups that could bind heavy metal ions through different mechanisms (Wan Ngah & Hanafiah, 2008; Abdel-Ghani et al., 2007).

Increase in adsorbate loading concentration has dual effects on the removal of the ions (**Figure 2**) such that at some lower concentrations the % adsorption increases with increase in concentration but it drops at higher concentrations. This phenomenon according to Adie et al. (2012) and Ibrahim and Jimoh, (2008) arises because at low loading concentration of metal ions, more binding sites are available, but as concentration increases the number of ions competing for available binding sites in the adsorbent increased. Also, at higher concentration, most of the ions are left unabsorbed due to saturation of the adsorption sites; and the ratio of surface active sites to ion concentration decreased with increasing metal ion concentration

and so ion removal reduced.

The adsorption envelope as presented in **Figure 3** shows that pH affects the solubility of metals in solution and also the adsorption behavior of ions on the functional groups of the adsorbents. The adsorption of Ni^{2+} and Cd^{2+} onto the two substrates increases from lower pH to a higher pH as a result of lowered competition between $H^+_{(aq)}$ and the metallic ions at the later condition. However, a reverse phenomenon was observed in the case of Cr(VI) adsorption for which it is higher at lower pH, a case similar to what has been reported elsewhere in the literature (Omar & Al-Itawi, 2007; Kehinde et al., 2009). Also the figure showed an increase in adsorption from MC to SD indicating variation in the surface active site of the two substrates.

In **Figure 4** the effects of increase in surface area of the adsorbents on their adsorption efficiencies was observed. In all cases the efficiency increased from the granular to the powdered form of the adsorbent.

A plot of the linear form of the Freundlich isotherm, $\ln q_e = \ln K_F + \ln C_e$ is presented in **Figure 5**, in which the slope $a = 1/n$ where n is the adsorption energetic and heterogeneity factor,

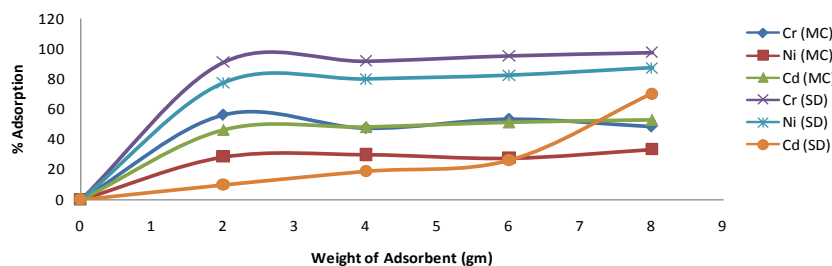


Figure 1. Variation of % adsorption with weight of adsorbent.

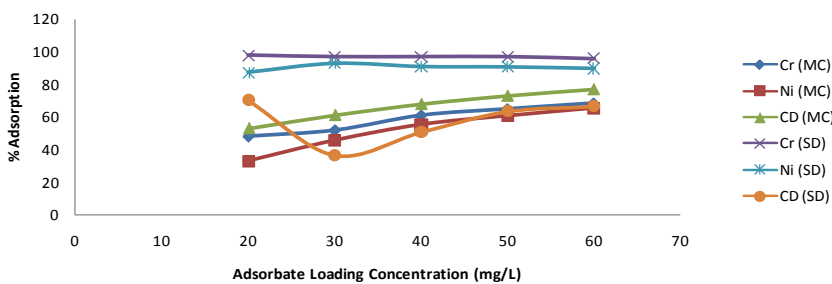


Figure 2. Variation of % adsorption with adsorbate loading concentration.

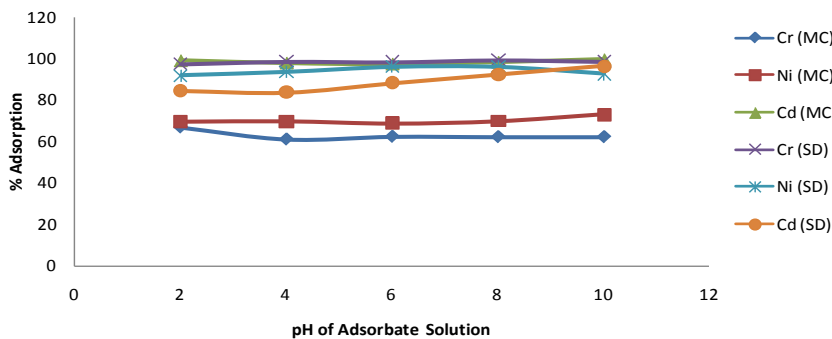


Figure 3. Variation of % adsorption with pH of the adsorbate solution.

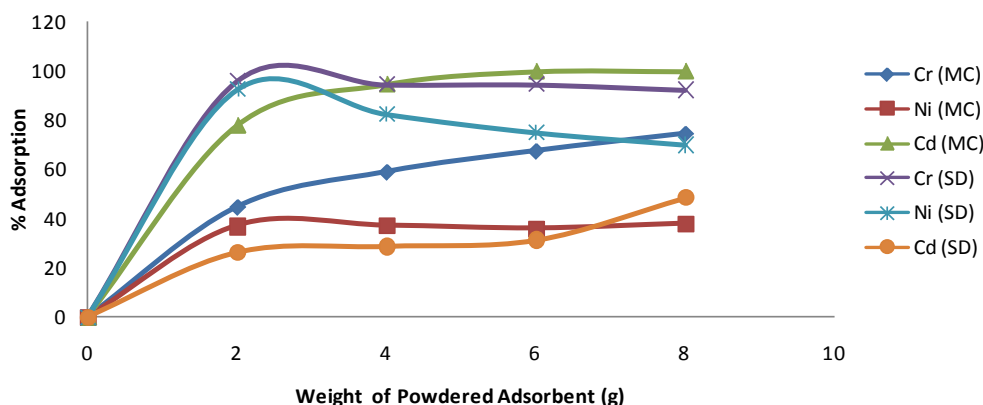


Figure 4.
Variation of % adsorption with weight of the powdered adsorbent.

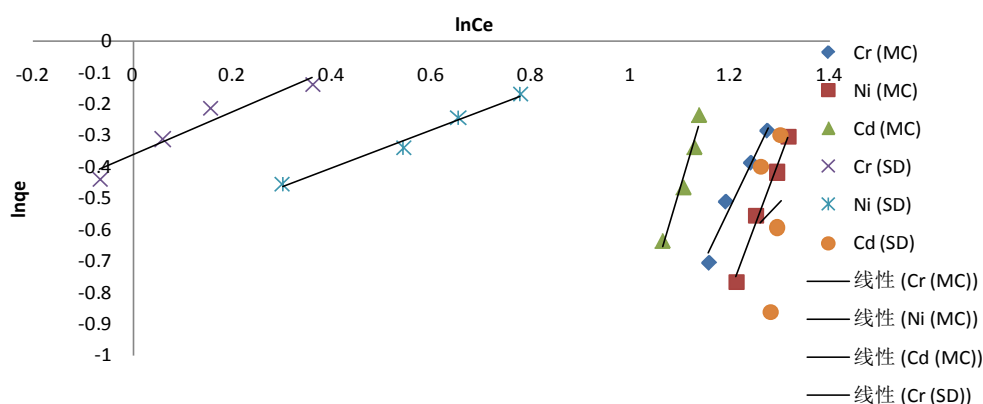


Figure 5.
Freundlich adsorption isotherm.

representing the deviation from linearity of the adsorption. While from the intercept, K_F is indicative of the relative adsorption capacity ($\text{mg}^{1-n} \cdot \text{L}^n \cdot \text{g}^{-1}$) of the adsorbent related to the bonding energy. From the n -values in **Table 1** it shows that the adsorption of Cr, Ni and Cd ions onto MC and for Cd ion onto SD (for which $n < 1$) is a chemisorption process, in other words, a localised monolayer adsorption. However, those of Cr and Ni onto SD (having $n > 1$) are favourable physisorption (multilayer) adsorption processes. On the other hand, **Figure 6** represents the Langmuir plot of the adsorption process, and from **Table 2** it can be understood that the adsorption of the three ions on MC; and those of Cr and Ni onto SD cannot be explained by the Langmuir isotherm, while that of Cd onto SD is linear indicating both chemisorption and physisorption are taking place at the same rate.

The thermodynamicity of the adsorption process is outlined in **Table 3**, from which the spontaneity (ΔS) and feasibility (ΔG) of the adsorption of the three metal ions onto MC varied as $\text{Cr} > \text{Cd} > \text{Ni}$. Whereas on SD the order is $\text{Cd} > \text{Ni} > \text{Cr}$.

Conclusion

The work highlighted the possibility of using the agricultural waste for the removal of the metallic ions from aqueous solutions with the adsorption nature varying from physical to chemical due to the differences existing in the binding nature of the adsorbates onto the two substrates.

Table 1.
Numeric constants for the adsorption of the metal ions onto the adsorbents.

Adsorbent	Ion	Freundlich		Langmuir	
		n_F	K_F	$q_m(\text{mg/g})$	$k(\text{L/mg})$
Maize Cob	Cr	.2967	.0103	500	-.0769
	Ni	.2319	.0025	500	-.0541
	Cd	.1872	.0018	100	-.1020
Sawdust	Cr	1.4514	.6949	-12.1951	-.1595
	Ni	1.6556	.5236	-71.4286	-.0718
	Cd	.5627	.0596	.0000	.0000

Table 2.
Variation of R_L for the various adsorbents with increase in initial metal ion concentration.

Co(mg/L)	Langmuir Separation Parameter (R_L)					
	Maize Cob			Sawdust		
	Cr	Ni	Cd	Cr	Ni	Cd
20	-1.8571	-12.333	-.9608	-.4565	-2.2941	1.0000
30	-.7647	-1.6087	-.4852	-.2641	-.8667	1.0000
40	-.4815	-.8605	-.3245	-.1858	-.5343	1.0000
50	-.3514	-.5873	-.2438	-.1433	-.3861	1.0000
60	-.2766	-.4458	-.1952	-.1167	-.3023	1.0000

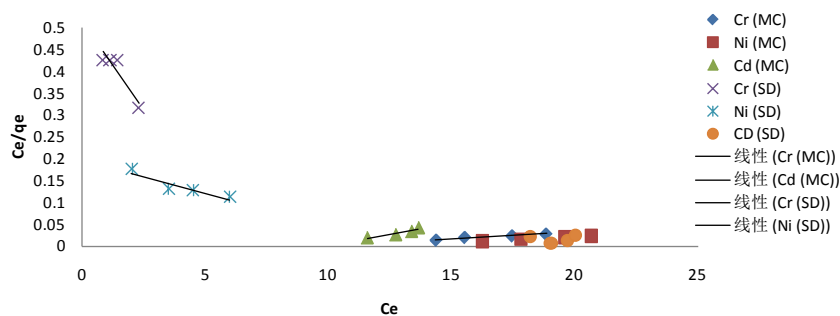


Figure 6.
Langmuir adsorption isotherm.

Table 3.
Thermodynamic parameters for the adsorption of the various metal ions.

Ions	Maize Cob				Sawdust			
	Ka	ΔG (Jmol ⁻¹)	ΔH (Jmol ⁻¹)	ΔS (Jmol ⁻¹ K ⁻¹)	Ka	ΔG (Jmol ⁻¹)	ΔH (Jmol ⁻¹)	ΔS (Jmol ⁻¹ K ⁻¹)
Cr	.0118	-3861.4	1466.5896	17.5841	.5708	6199.57	-566.8485	-22.3314
Ni	.0062	-1167.32	1271.2106	8.0480	.0875	3055.09	256.3206	-9.2369
Cd	.0143	-2977.67	1347.6994	14.2751	.0299	-406.07	888.7666	4.2734

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

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