Thermodynamics of the adsorption of cadmium ions by natural lateritic soil

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Abstract

Adsorption is a major process responsible for accumulation of heavy metals which in turn leads to an increase in health hazards. Understanding absorption process of these heavy metals is crucial for the assessment of their fate and reclamation in polluted soils. In this study, the sorption mechanism of cadmium metal on lateritic soil was evaluated at two temperatures (298K and 323K) using the batch method. The lateritic soil samples used were collected from Ilaro, Ogun State. The Langmuir and Freundlich isotherms were used to describe the adsorption of the metal ion. Results of thermodynamic parameters revealed that the equilibrium constant (Keq) decreased with increase in temperature. The small but positive value for the free energy (ΔG) indicated that the absorption of cadmium ion on the soil was spontaneous. The enthalpy of the reaction (ΔH) was negative implying that the aborption of this metal ion is exothermic. The positive value ($63.23 Jmol^{-1}$) of the entropy of reaction, ΔS is an indication of disorder in the cadmium sorption process in the soil which leads to an increase in the degree of randomness at the surface of the soil which in turn results to an increase in the adsorption capacity of the ion in the soil.

Keywords: Cadmium, Sorption, Freundlich, Langmuir, isotherms and thermodynamic

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Introduction

A major challenge facing most countries in tropical areas is how to increase the capacity of their soils to produce enough food and fibre on sustainable basis to support their ever growing population. Some practices like application of fertilizers, farmyard manure are employed without due regards to the long term fate and reactions of these amendments in the receiving soils. Also, with the drive towards rural transformation, municipal, industrial and domestic wastes which may be laden with toxic heavy metals like cadmium (Siegel, 2002) are frequently dumped freely on land.

Furthermore, mining and industrial activities have caused extensive heavy metal contamination by introducing heavy metals directly into the surrounding environment (Ernst, 1995; Li and Li, 2001; Al-Juboury, 2009; Ahmad *et al.,* 2010). Cadmium ions constitute one of the contaminant groups considered noxious to human health and are commonly found in soils and plants (Salim and Munekage, 2009). A major challenge with many heavy metals like cadmium is their non-biodegradability, thus leading to bioaccumulation and persistence. A question that needs to be answered is how such polluted soils can be remediated.

Adsorption techniques are common ways to remediate these polluted soils. These techniques have been popular in recent years due to their simplicity as well as the availability of a wide range of adsorbents. Several workers have used a variety of low-cost natural and synthetic adsorbents (Gupta *et al*., 2005) as well as of biomaterials (Bhatnagar *et al*., 2002; Gamode *et al*., 2004).

Lateritic soils have been used by some research groups in removing priority inorganic pollutants from water (Sarkar *et al*., 2004). The presence of silica, alumina and metal oxides in lateritic soils, makes them good adsorbents. In this study, the suitability of naturally occurring, low cost lateritic soil is explored as potential heavy metal adsorbent. This study was also undertaken to predict the sorption behaviour of cadmium ions and to determine the different thermodynamic parameters of the adsorption system.

Adsorption studies over a range of operating conditions were used to evaluate the effectiveness of lateritic soil as an adsorbent in the remediation of soils polluted with heavy metals. Langmuir and Freudlich isotherms were examined and the thermodynamic parameter calculations were carried out to have more insight into the process. The isotherms examined were used to establish the equilibrium and determine the conditions for maximum cadmium ion removal over the soil surface at 298K and 323K. Such information on heavy metal sorption is lacking in this part of the world and so this study was undertaken to predict the sorption behaviour of cadmium ions using the adsorption isotherms and to determine the different thermodynamic and sorption parameters as influenced by major properties of the soil in question.

Materials and Methods

The soil samples were obtained from Ilaro, Ogun State, Nigeria. Composite samples were made from five randomly collected soils from the surface horizons. The samples were air dried for about two weeks and passed through a 2mm sieve to remove plant materials and stored in polythene bag.

The physicochemical parameters were carried out using the method of Udo, E.J, 1986 culled from the ‘Laboratory Manual for the Analysis of Soil, Plant and Water Samples. The pH of the soil was determined in water and 1.0M KCl (in a ratio 1:2) with a glass electrode pH meter. The organic carbon and the particle size analysis were determined by the Walkey-Black wet oxidation method (Nelson and Sommers, 1996) and the international pipette method (Gee and Bauder, 1986). The exchangeable acidity and bases were determined using the titration method and the cation exchange capacity was determined by the summation method of adding the total exchangeable bases and the total exchangeable acidity.

1000pm of cadmium stock solution was prepared by dissolving 2.744g of the cadmium salt, Cd $(N0_3)_2.4H_20$ in deionized water and made to mark in a 1 Litre volumetric flask. Working standards of 0, 2, 4, 8, 15, 30, 45, 75 ppm respectively were prepared by diluting the stock solution appropriately.

For the thermodynamic studies, 1.00g of the soil sample was weighed into eight pairs of 100ml plastic bottles. The plastic bottles had been previously soaked in concentrated HNO_3 for 12 hours, washed thoroughly with tap water and then with distilled water. The bottles were labelled according to the concentration of the metal to be added (0, 2, 4, 8, 15, 30, 45 and 75mg/L). The pH of the soil suspension before and after the shaking process was adjusted with dilute HCl/NaOH to the original soil pH as that of control treatment. The bottles were then shaken for eight hours using an electrical orbital shaker.

Each solution was filtered and the filtrates kept for metal analysis using the Atomic Absorption Spectrophotometer, AAS (Model: 210 VGP)

The amount of heavy metals adsorbed by the soil was calculated from the difference between the initial concentration and the final concentration of the metals in the equilibrium solution using the relationship below:

$$q_e = \frac{(C_0 - C_e)}{W} \;x\; \frac{V}{1000}$$

Where q_e = the amount of metal of metal ion adsorbed on the soil surface (mg/g)

C_0 = the initial metal ion concentration (mg/L)

C_e = the equilibrium metal ion concentration (mg/L)

V = volume of metal ion in solution (ml)

W = weight of the soil sample (g)

The equilibrium data were then fitted to the Langmuir and Freundlich isotherm models that are used frequently to describe equilibrium adsorption data by plotting the curves of the equations below:

$$1/q_e = (\, 1/QbC_e) + 1/Q \qquad \text{Langmuir}$$

Where q_e is the amount of solute adsorbed (mg/g) at equilibrium and C_e is the equilibrium solute concentration (mg/L) in solution. The values of the empirical constants Q and b, denoting the monolayer capacity and energy of adsorption, respectively are evaluated from the slope and intercept of the linear plot of $1/q_e$ against $1/C_e$.

$$\ln q_e = \ln K_f + (\, 1/n) \ln C_e \qquad \text{Freundlich}$$

A linear plot of $\ln q_e$ against $\ln C_e$ yields a slope of 1/n and intercept of $\ln K_f$. the value of K_f is an indication of adsorption capacity and the value of 1/n indicates the adsorption intensity.

Thermodynamic parameters were calculated from the variation of the thermodynamic equilibrium constant, K^0, computed by following the procedure outlined by Biggar and Cheung (1973). The value of K^0 for the adsorption reaction can be described as:

$$K^0 = Cs / Ce$$

The values of K^0 were obtained by plotting Cs vsCe and extrapolating to zero Cs. The standard free energy (ΔG^0) was calculated as:

$$\Delta G^0 = -RT\ln K^0$$

The enthalpy change for the metal ion was evaluated from the integrated Van Hoff equation:

$$\ln\frac{K_2}{K_1} = \frac{H}{R}\left[\frac{1}{T_2} \quad \frac{1}{T_1}\right]$$

Where K_2 and K_1 are equilibrium constants for the metal ion at $T_2$and T_1 respectively and R is the gas constant and it is equal to 8.3145. The entropy changes of the metal ions were then calculated from the relationship below:

$$\Delta S^0 = \frac{\Delta H^0 - \Delta G^0}{T}$$

Table 1: physicochemical parameters of the soil as determined in the laboratory

Property	Values
pH (1:2, laterite:water mixture)	5.9
pH (1:2, laterite:KCl mixture)	4.7
Organic carbon (%)	2.17
Organic matter (%)	3.74
Exchangeable acidity	0.40
% Clay	30.80
% Silt	22.00
% Sand	47.20
Exchangeable cations (Cmol/Kg)	
K	0.16
Na	0.86
Mg	0.79
Ca	2.41
Base saturation (%)	91.34
CEC (Meq/100g)	4.62
ECEC (Meq/100g)	4.62
Hydraulic conductivity (cm/min)	0.746

Results and Discussion

The physicochemical properties of the soil as determined in the laboratory are shown in table 1. The pH of the laterite soil sample measured in the ratio 1:2 of the soil to deionized water and 1 molar KCl was 5.9 and 4.7 respectively. This is an indication of slightly acidic soil. The reason might not be unconnected with the elements in the primary rock minerals released and their reactions in aqueous solution. Similar results have been reported by Udoeyo *et al* (2010) for Imo lateritic soils and Maji *et al* (2007). The lower pH value of the soil sample in 1M may not be unconnected to the fact that the potassium ion displaces the hydrogen ions from the soil's cation exchange site thereby giving it a lower value (Olu-Owolabi *et al*., 2010).

The organic matter content of the soil sample was found to 3.74%. This might be due to the accumulation of organic matter over the years as a result of its location. This accumulation in the soil is favoured by high rainfall, low temperature, native grass vegetation and poor drainage (Ministry of Environment, Ogun State, 2006). This value is however, a characteristic of many soils in Nigeria (Sha'ato, 1996). The organic carbon in the soil was found to be 2.167%. This is an indication of the decomposable organic matter in the soil (Page, 1982). Similar values were reported by Adhikari *et al* (2003), Udoeyo *et al* (2010) and Abhijit *et al* (2007). The relationship of these values with that of this work is attributed to the tropical climatic conditions of the sampling areas.

The particle size analysis showed that the soil had a high amount of sand followed by clay and silt. The percentage sand and silt (47.2 and 22.0%) reflects that of the parent rock. Being located in the tropics, the sand and silt particles are composed of aluminium and iron oxides and hydroxides dominate in these fractions as a result of more intense weathering (Udoeyo *et al,* 2010). The percentage clay is an indication that the soil is composed mainly of clay minerals and humic substances which facilitated the decomposition of organic matter.

The soil sample showed an appreciable amount of the exchangeable bases such as Mg, Ca, K, Na (Table 1). The exchangeable calcium was the highest compared to the other exchangeable cations. The lower value of K is an indication that the site from where the soil was taken is unfertilized and the result obtained from this work agreed with that of Banjoko, *et al* (1983) in some soils in southern Nigeria.

Mathematical Modelling of the Adsorption Isotherm

The ability of the soil sample to adsorb cadmium from aqueous solution is evaluated from the general nature of the adsorption isotherm plot (Ce against qe) as shown in fig 1. The shape of the isotherm gives an indication of whether the adsorption is favourable or unfavourable as indicated by Webber and Smith (1987).

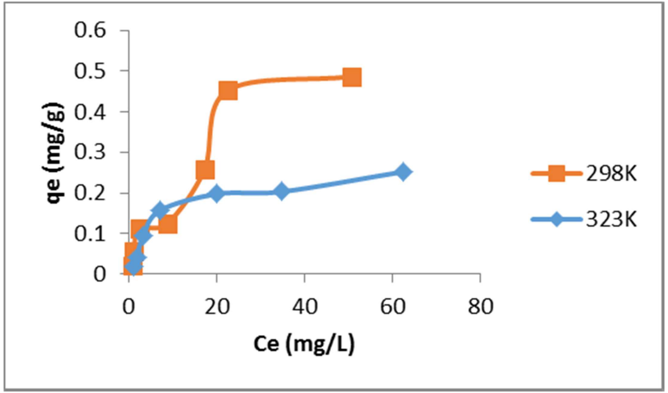

Fig 1: Model graph for the adsorption of Cd^{2+} on lateritic soil at 298K and 323K

The L-type nature of the curve obtained suggests favourable adsorption and also a strong tendency to the monolayer formation. It is an indicative of an ion with relatively high affinity for the exchanger. Similar results were reported by Sarkar *et al.* (2006), and Abhijit *et al.* (2007). The adsorption sites, however, are gradually filled as concentration is increased and subsequent adsorption becomes difficult thereby limiting the extent of adsorption (Sarkar *et al.*, 2002).

The sorption was fitted to the Langmuir and Freundlich isotherm models that are used most frequently to describe equilibrium adsorption data. The adsorption parameters determined from both the Langmuir and Freundlich plots for cadmium is shown in table 2 and their plots at 298K and 323K are shown in fig 2.

Langmuir	Freundlich

	Q(mg/g)	b(mg/L)	R^2	K_f	n	R^2
298K	1.481	0.021	0.797	0.039	1.466	0.889
323K	8.700	0.002	0.875	0.024	1.538	0.878

Table 2: Adsorption parameters determined from both the Langmuir and Freundlich plots for cadmium metal

Dose: 1.0g; pH: 6.0; Conc: 4-90ppm; Speed: 200rpm; Particle size: 0.5mm

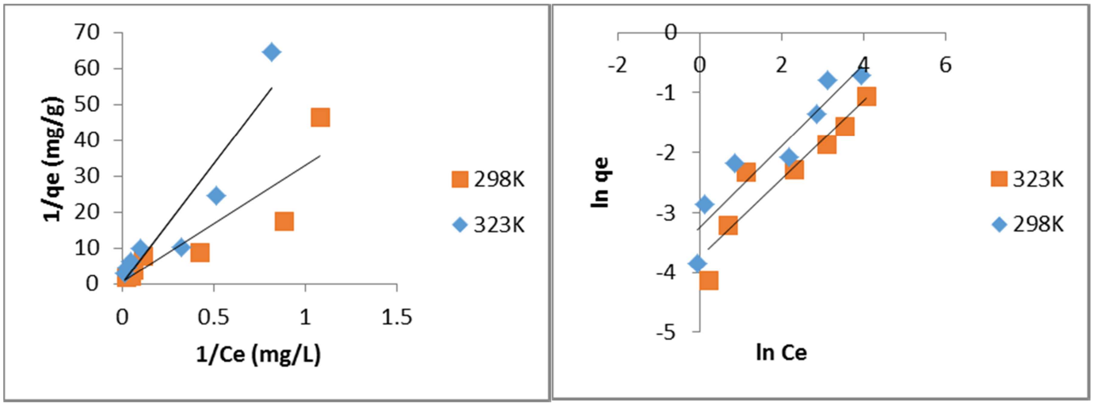

Fig 2: Langmuir and Freundlich plot for the adsorption of cadmium over lateritic soil at 298K and 323K

Judging from the R^2- values, the adsorption of cadmium fitted more to the Freundlich isotherm at both temperatures with R^2-values of 0.889 and 0.878. Similar results were obtained by Udoeyo *et al.* (2010) for Imo lateritic soils.

The monolayer sorption capacity (Q) which is a measure of the maximum adsorption capacity corresponding to complete monolayer coverage showed that the soil sample had adsorption capacities of 1.481 and 8.700 mg/g for cadmium at 298 and 323K respectively showing affinity for the ion at higher temperature. This can be explained to be due to the small ionic radii of the metal. This trend has been supported by several workers following the Pauling ionic radii of different metal- Abia *et al* (2002), Horsfall and Abia (2003), Horsfall and Spiff (2004). The values of Q and b denoting adsorption capacity and energy of adsorption are indications of preference of the soil sample for the metal in the soil (OluOwolabi *et al*, 2010).

K_f is the relative adsorption capacity and 1/n indicates the adsorption intensity i.e the ease of separation of the metal ion from its adsorbent. The K_f values of Cd^{2+} at 298K and 323K are 0.039 and 0.024. This shows that cadmium has some adsorptive tendency towards the lateritic soil surface. The Freundlich equation parameter, 1/n, which is a measure of the adsorption intensity was 0.682 and 0.650 respectively at both temperatures. This revealed a decrease in the adsorption intensity with increase in temperature. Also, according to Kairvelu and Namasivayan (2000), n values between 1-10 represent beneficial adsorption and a close look at the present study showed n-values of 1.466 and 1.538 indicating that the adsorption of cadmium on lateritic soil is beneficial and also showing that the Freundlich equation is suitable for highly heterogeneous surfaces.

The separation parameters for cadmium investigated on lateritic soil is less than unity at 298K (0.856) and approximately 1.00 at 323K. This indicates that the lateritic soil has favourable isotherm at 298K and a linear relationship at 323K (1.013) and hence, the soil is an excellent adsorbent for cadmium ion (Sha'ato, 1996). Similar results were obtained by Sarkar *et al* (2004) and Maiti *et al* (2007) who also predicted favourable adsorption based on r-values obtained which fell within 0-1.

In comparing both isotherms, the linear regression values indicate that the Freundlich isotherm was best suited to predict the fate of cadmium though the positive values obtained for the isotherm constants implies that the two considered are suitable for the explanation of the adsorption process of cadmium ion. The soil, thus, may be used as a lining material under landfills to adsorb the heavy metals so that the ground water resources could maintained safely (Udoeyo *et al*, 2010).

Evaluation of Thermodynamic Parameters

Evaluation of thermodynamic parameter provides an insight into the mechanism of cadmium in the soil. In order to study the feasibility of the process using the lateritic soil sample, the free energy change (ΔG^0) of the process was calculated from the equilibrium constant obtained from the plot in fig 3.

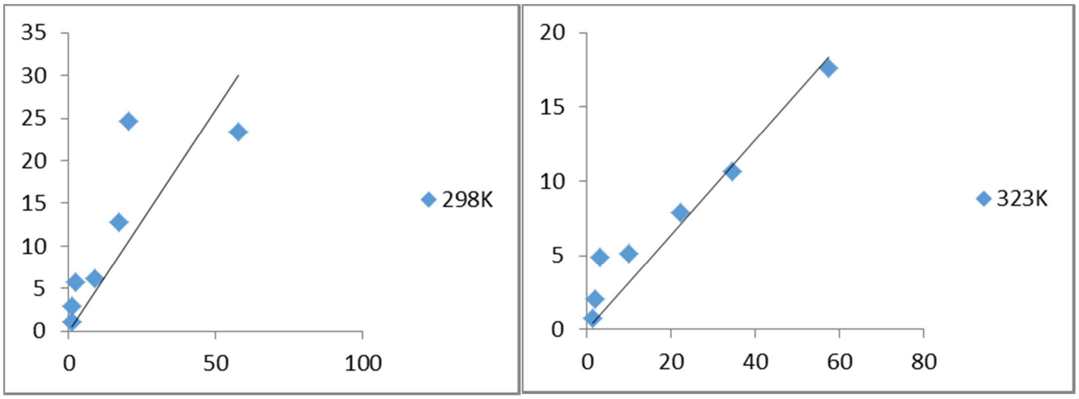

Fig 3: Plots Cs vsCe in the determination of equilibrium constant for cadmium ion at 298K and 323K
Keq= 0.577 **Keq= 0.319**

Table 3 shows that there was a decrease in the equilibrium constant (Keq) with increase in temperature from 298K to 323K. This implies that a rise in temperature encouraged the exchange in favour of the cadmium ion adsorption by the soil.

Table 3: Thermodynamic parameters of cadmium ion sorption in the soil

Temp(K)	**Keq**	**ΔG(KJmol^{-})**	**ΔH(KJmol^{-1})**	**ΔS(Jmol^{-1})**
298	0.57	1.36	-18.97	68.23
323	0.31	3.09		

The Keq values obtained were positive at both temperatures indicating that the exchange reactions were favoured to an extent and equally feasible.

The Gibb's free energy for cadmium ion was positive, 1.36KJmol^{-1} and 3.09KJmol^{-1} at 298K and 323K respectively (Table 3). Though a negative value implying that the driving force for the formation of a complex is favoured was expected to show greater sorption (Adhikari *et al.*,2003), small positive values for ΔG as observed in this study can also be explained. A plausible explanation may be the uncertainties in the estimation of thermodynamic parameters using linear plots of thermodynamic models. Some errors may be introduced that could shift values from the border of one extreme to another (Unuabonah *et al.*, 2008). When this occurs, adsorption reactions that have small but negative ΔG could shift to small but positive ΔG. This may be the case for the positive ΔG values obtained in this study, though Ozcan and Ozcan (2004) have shown that positive values for ΔG are quite common with ion-exchange mechanism of adsorption of cations. The ΔG values obtained for cadmium ion implies that the reaction was feasible.

The enthalpy change for cadmium was observed to be -18.973KJmol^{-1}. This is an indication that the sorption reaction of cadmium was exothermic. From earlier results, the reaction of cadmium ion was exothermic and favourable owing to the small positive values of the free energy.

It can be seen that the above reaction was favoured by high temperature though the values of ΔH^0 obtained from the plots of linear K^0 versus 1/T was linear at both at both temperatures and this indicates that the mechanism of adsorption is not changed as temperature is increased but the supply of thermal energy is different (Hosseinpur, 2010). In general, the nature of the adsorption process for Cd^{2+} shows that the process is energetically stable (Biggar and Cheung, 1973)

The value for ΔS^0 was found to be 63.23Jmol^{-1}. This is indicative of disorder in the Cd^{2+} sorption process in the soil which leads to an increase in the degree of randomness at the surface of the soil during the adsorption process of the ion (Hosseinpur, 2010). The increase in the randomness leads to an increase in the adsorption capacity of the ion on the soil (Abou-Mesalam, 2003). The overall entropy change favoured adsorption of the Cd^{2+} (table 5) and this represented the major force leading to observed spontaneity of the exchange. Thus, the withdrawal of the metal ions from the solution with concurrent replacement with ions in solution has led to a comparatively less ordered arrangement of the solution phase, reflected in the increase in entropy.

Conclusion

The result of this study indicates that from the sorption isotherms, the adsorption capacity of the soil for Cd^{2+} increased with increase in temperature and also implies high affinity of Cd^{2+} to the soil exchange sites. Thermodynamic results revealed that the adsorption of

Cd^{2+} on the soil's exchange sites was feasible and spontaneous while enthalpy change was exothermic. Thus for developing suitable strategies for the proper management of cadmium metal pollution, lateritic soil and its conditions particularly temperature needs to be considered.

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