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Sorption and Desorption of Competing Heavy Metalsfrom Laterite

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Abstract

Heavy metal pollution is a major concern for environmentalists. Competing ions affect the sorption of heavy metals onto the surfaces of soils. This study evaluated competitive adsorption and desorption of Cd, Cr, Pb, Cu and Zn from two laterite samples – Emuhu Laterite, LAEM and Abeokuta Laterite, LAAB, obtained from Nigeria. The equilibrium concentrations of heavy metals following adsorption using mixed metal solutions were determined. Desorption studies were performed using residues of adsorption studies. Laterite affinities for heavy metal adsorption/desorption were determined by means of selectivity sequences. The adsorption sequences obtained were Cu >Pb> Cr > Zn > Cd and Cu > Cr >Pb≫ Zn > Cd for LAEM and LAAB, respectively, while the sequences for the desorption experiments were Cr > Cu >Pb> Zn > Cd and Cr≫Cu >Pb> Zn > Cd, respectively. Cr, Pb, Cu were strongly adsorbed by both soils. Adsorptions of the heavy metals on LAEM and LAAB fitted into the Freundlich and Langmuir isotherm model, respectively. The results suggested that the two soils are capable of receiving and holding Cr, Pb and Cu pollutants in solution. They can thus be recommended for remediation of the three metals from industrial waste effluents.

Keywords: Adsorption, Competition, Heavy Metals, Selectivity, Laterite, Isotherms

Background to the Study

The increasing levels of toxic heavy metal ions discharged to the environment have received considerable attention due to the adverse effects on the environment. These ions are a hazard to public health and the environment when discharged inappropriately(Laus, Costa, Szpoganicz & Favere, 2010) because in contaminated habitats, they may accumulate in microorganisms, aquatic flora and fauna, which in turn, mayenter into the human food chain and result in health problems (Sarabjeet & Dinesh, 2007; You, Tsai & Huang, 2009). The potential sources of heavy metal ions in wastewaters are diverse (Yilmaz 2009). Removal of heavy metals from industrial wastewater is therefore of primary importance. To mitigate the heavy metal pollution, several methods have evolved over the years (Merzouk, Gourich, Sekki, Madani & Chibane, 2009; Wang et al., 2006).The most commonly used traditional treatment technologies (Ozsoy & Kumbur, 2006) have several disadvantages, including high operational cost, incomplete metal removal, low selectivity, high energy consumption and the generation of a large amount of toxic sludge or other products to be disposed off (Xu, Liu & Tay, 2006; Bhatnagar & Silanpaa, 2010). These disadvantages of conventional systems, together with the need for more economical and effective methods for the removal of metals from wastewaters, have resulted in the development of new separation technologies. Adsorption as a treatment process, has attracted considerable interest and appears to be the most widely used (Srivastava , *Mall & Mishra,* 2009; Adebowale, Unuabonah & Olu-owolabi, 2008). It is a user-friendly technique and seems to be most versatile and effective if combined with appropriate regeneration steps. Most favoured adsorbents are those that are available in large quantities, cheap, widely available and are environmentally friendly. Natural materials therefore, are of interest of which parts of the agricultural products that have no food value are prominent.

Despite the over-whelming advocacy and use of the agricultural wastes as adsorbents, they are not without disadvantages. The application of untreated plant wastes as adsorbents brings several problems such as low adsorption capacity, high chemical oxygen demand (COD) and biological chemical demand (BOD) as well as total organic carbon (TOC) due to release of soluble organic compounds contained in the plant materials (Nakajima & Sakaguchi, 1990).Therefore, plant wastes need to be modified or treated before being applied for the decontamination of heavy metals. Therefore, there is a need to source for other materials of the aforementioned biosor bent properties but without the problem of disposal. Of relevance in this case is laterite – a wide variety of red, brown, and yellow, fined grained residual soils of light texture as well as nodular gravels and cemented soils, which gathers on the surface of rocks from which it is produced by decomposition and is common in the tropical regions. Being a naturally abundant, cheap, and environmentally friendly material, its suitability for use for heavy metal remediation cannot be over emphasized, putting into consideration problems associated with aforementioned adsorbents. To the best of our knowledge, no work has been done in this regard. The objective of this study therefore, was to evaluate competitive adsorption and desorption of Cd, Cr, Pb, Cu and Zn ions from two laterite samples obtained from Nigeria.

Materials and Methods

Soil Sampling and Sample Pre-treatment

Laterite was collected from the non-vegetative layer (30-50cm) of a laterite site from Oke-Imosan, (Lat. 7° 7' 0N, Long. 3° 22' 0E) Abeokuta, Ogun State and Emuhu (Lat. 6° 16' 19N, Long. 6° 15' 44E), Ika South LGA of Delta State. Samples were collected with soil auger and stored in polyethylene bags which were properly labelled for easy identification as LAAB and LAEM, respectively. They were air-dried, ground and sieved through 1.0mm mesh and stored for analyses.

Physicochemical Parameters of Soil

The soil pH was measured with a glass-electrode pH meter in 1:1 soil to water and soil to 1M KCl. The organic carbon and organic matter was determined by the wet oxidation method of Walkley and Black (1934) and Jackson (1958). Particle size distribution was measured by the hydrometer (Day, 1965, Juo, 1979). The exchangeable bases were extracted with 1M NH_4OAc (pH 7) (Thomas, 1982). The metal oxides were determined using X–ray Fluorescence Spectrometer Model ARL-9900, OASIS at 40kV, 30mA.

Competitive Adsorption

The adsorption and desorption capacities of the laterite samples were determined in duplicate using the method of Xiong*et al.* (2005) with modifications. Adsorption and desorption distribution coefficients of each metal in each soil at equilibrium were calculated from the results of experiments using the equation:

$$K_d = \frac{q_e}{C_e}$$

K_d is the Distribution Coefficient, q_e is the amount of metal adsorbed by laterite (mg/g), C_e is the amount of metal unadsorbed in solution at equilibrium (mg/L).

Sorption and desorption data were characterized by the Langmuir and Freundlich isotherm models. For the linear form of the Langmuir model, plots of C_e/q_e against C_e were made using

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

Where q_e is the amount of metal adsorbed by laterite (mg/g), q_m is the maximum adsorption capacity of adsorbent (mg/g), K is the equilibrium constant of Langmuir Isotherm (mg/g), and C_e is the amount of metal unadsorbed in solution at equilibrium (mg/L).

For the Freundlich models, plots of log q_e against log C_e were made using the linearised equation:

$$\log q_e = \log K_F + 1/n \log C_e$$

Where q_e is the amount of metal adsorbed by laterite (mg/g), C_e is the amount of metal unadsorbed in solution at equilibrium (mg/L), K_F is the mono-component constant of Freundlich isotherm of the single-component (mg/g) and n is the mono-component Freundlich heterogeneity factor of the single component.

Statistical Analyses

The mean values of all determinations and all other statistical analyses were performed using Windows Microsoft Excel version 2007.

Results and Discussion

The results of the physicochemical analyses of adsorbed and desorbed metals are presented in Tables 1.

The physicochemical analyses revealed that the two soils studied, Abeokuta laterite (LAAB) and Emuhu laterite (LAEM), had pH values in the acidic range. The pH of LAAB in deionised water and KCl solution were 4.5 and 3.8 while those of LAEM were 5.3 and 4.6, respectively. A value of -0.7 for ΔpH ($pH_{KCL} – pH_{H2O}$) was observed for both soils, which means that a slight negative charge was present in both soils at the equilibrium pH (Cazangaet al., 2008). These suggested that H^+ on the soils were replaced by metal ions in solution. Soil pH affects heavy metal savailability in soil. Availability is relatively low when pH is around 6.5 to 7. The mobility of trace elements is reduced with increasing soil pH because of the precipitation as insoluble hydroxides, carbonates, and organic complexes (Silveira, Alleoni & Guilherme, 2003). With the low pH value of the soil, heavy metal mobility will be high and metal availability may be low.

The organic matter and thus the organic carbon contents of the soils were low – 0.1% and 0.6%, respectively, in LAAB and 1.5×10^{-3}% and 0.09%, respectively, in LAEM. With the low values, the soils are not expected to support vegetation and would be expected to have low sorption abilities for metals. The cation exchange capacity, CEC, of both soils reflected the low organic matter contents. CEC values of 3.82 (meq/100g) and 4.12 (meq/100g) were obtained for LAAB and LAEM, respectively. The order of decrease in exchangeable bases contents were in the order Ca> Na > Mg > K in both soils. Calcium, the dominant exchangeable base in both soils, accounted for 27.75% and 30.10% of CEC in LAAB and LAEM, respectively.

Although, LAEM had a lower organic matter than LAAB, its higher CEC may be attributed to the clay content which was 38.1%, an order of 15.3% greater than the 22.8% recorded for LAAB. Higher sand contents of 71.20% and 55.20% were recorded for LAAB and LAEM, respectively. The silt contents of the two soils were however the same, 6.00%.

Table 1: Physicochemical Properties of Abeokuta and Emuhu Laterites*

Parameters		LAAB	LAEM
pH	In Water	4.5	5.3
	In KCl	3.8	4.6
Organic Matter (%)		0.10	1.5×10^{-3}
Organic Carbon (%)		0.60	0.09
Total nitrogen (%)		0.15	0.02
Exchangeable bases (mg/100g) -			
Ca		1.06	1.24
Mg		0.57	0.54
Na		0.75	0.87
K		0.04	0.07
Exchangeable Acidity (meq/100g)		1.40	1.40
Cation Exchange Capacity (meq/100g)		3.82	4.12
Base Saturation (%)		63.35	66.02
Particle Size Distribution (%)			
Sand		71.20	55.20
Silt		6.00	6.00
Clay		22.8	38.1
Exchangeable Micronutrients (mg/kg)			
Cu		0.60	0.95
Zn		1.19	1.37
Mn		1.60	2.30
Fe		11.20	20.20
SiO_2 (%)		70.33	67.70
Al_2O_3 (%)		17.58	17.20
Fe_2O_3 (%)		5.91	6.10
CaO (%)		2.46	1.75
MgO (%)		1.37	1.23
Na_2O (%)		0.02	0.02
K_2O (%)		0.29	0.35
SO_3 (%)		0.04	0.03
Silica Ratio (%)		2.99	2.91
Aluminium Ratio (%)		2.98	2.82
$CaCO_3$		4.4	3.12

* Values are Mean of Duplicate Determinations

The initial desorption studies on the soil samples using the background electrolyte only revealed that no significant amounts of heavy metals were desorbed from the laterites. The data obtained in the adsorption and especially the desorption experiments were not affected by presumed heavy metal likely to be leached from the laterites.

Table 2 shows the equilibrium concentrations, Ec, and the amount of adsorbed metal cations in the supernatant after the adsorption experiment. A general trend was followed by both soils. For the concentrations applied, the Ec were relatively low for Cr, Pb and Cu. These showed affinities of the metal cations for the soil surfaces while Cd and Zn had low affinities for the surfaces. An irregular trend in the amounts of metal cation adsorbed was observed as the concentrations of applied metal cations increased. However, the higher values observed for Cr, Pb and Cu were maintained. The behaviour may be explained in terms of the type of metal-surface interaction (McBrides, 1984). Zn and Cd retention is more dependent on covalent interactions with the mineral structures. This reasoning finds support also in the results of Berti and Jacobs (1996); Fontes, De Matos, Da Costa & Neves(2000); Gomes et al. (2001), who found that simultaneous competition in soils normally, favour Cr, Pb and Cu, as compared to Zn, Cd and Ni. From Table 4, the sum of equilibrium adsorbed metal ions was generally high with LAEM than LAAB. The trends of adsorption observed for the two soil samples were the same with Cu >Pb> Cr > Zn >Cd. In the desorption studies, irregular desorption patterns were generally found for the heavy metal cations (Table 3). Irregularities in sorption and desorption experiments may be attributed to the complex effects of competition for binding sites and other interactions between ions (Vega, Covelo & Andrade, 2006). However, to a large extent, higher Ec values were accompanied by high amounts of desorbed metal cations (Des). The sum of metal ion desorbed were generally high with LAEM than LAAB. The trends of desorption of metal cation were Cr < Cd < Cu <Pb< Zn and Cr < Cd <Pb< Cu < Zn for LAEM and LAAB, respectively, with Cu and Pb changing positions. The lower values of desorbed metal cations reflect a high tendency of metal retention on the soil. However, the low values obtained for Cd should not be confused for high affinities, bearing in mind that low amounts of Cd were adsorbed in the adsorption studies.

Table 2: Equilibrium Concentration (Ec (mg/L)) and Metal Cation Adsorbed (Ads (mg/g)) from the Solution

Table 2 Equilibrium Concentration (Ec (mg/L)) and Metal Cation Adsorbed (Ads (mg/g)) from the Solution

Soil	Concentration Added (mg/L)	Metal Cation									
		Cd		Cr		Pb		Cu		Zn	
		Ec (mg/L)	Ads (mg/g)	Ec (mg/L)	Ads (mg/g)	Ec (mg/L	Ads (mg/g)	Ec (mg/L	Ads (mg/g)	Ec (mg/L	Ads (mg/g)
LAEM	100	97.25	0.03	39.24	0.61	55.60	0.44	64.13	0.36	83.63	0.16
	200	198.50	0.02	131.93	0.69	130.00	0.70	82.63	1.17	193.25	0.07
	300	296.75	0.03	232.25	0.68	191.00	1.09	194.63	1.05	288.00	0.12
	400	391.40	0.09	330.80	0.69	266.00	1.34	222.25	1.78	319.88	0.80
	500	482.50	0.18	413.50	0.87	345.00	1.55	352.1	1.48	467.38	0.33
LAAB	100	98.25	0.02	34.64	0.65	59.45	0.41	69.13	0.31	86.93	0.13
	200	195.75	0.04	142.75	0.57	138.70	0.61	79.63	1.20	189.50	0.11
	300	294.00	0.06	223.80	0.76	164.50	1.36	169.50	1.31	282.75	0.17
	400	394.75	0.05	320.95	0.79	263.50	1.37	220.75	1.79	327.63	0.72
	500	492.50	0.08	428.88	0.71	391.75	1.08	440.88	0.59	476.00	0.24

Table 3 Equilibrium Concentration (Ec (mg/L)) and Metal Cation Desorbed (Des (mg/g)) from the Solution.

Soil	Concentration Added (mg/L)	Metal Cation									
		Cd		Cr		Pb		Cu		Zn	
		Ec (mg/L)	Des (mg/g)	Ec (mg/L)	Des (mg/g)	Ec (mg/L)	Des (mg/g)	Ec (mg/L)	Des (mg/g)	Ec (mg/L)	Des (mg/g)
LAEM	100	0.70	0.03	0.31	0.01	0.74	0.03	0.85	0.03	1.36	0.05
	200	0.23	0.01	0.17	0.01	1.25	0.05	1.16	0.05	0.77	0.03
	300	0.38	0.03	0.24	0.01	2.43	0.09	1.55	0.06	2.48	0.10
	400	0.30	0.08	0.30	0.01	6.16	0.24	2.67	0.11	6.34	0.25
	500	0.08	0.16	0.43	0.02	5.43	0.21	4.51	0.18	5.64	0.22
LAAB	100	0.44	0.02	0.05	2 x 10^{3}	0.53	0.02	0.34	0.01	1.01	0.04
	200	0.71	0.04	0.16	0.01	1.26	0.05	1.54	0.06	1.77	0.07
	300	0.73	0.06	0.17	0.01	1.26	0.05	1.80	0.07	3.17	0.12
	400	0.29	0.05	0.06	2 x 10^{-3}	2.41	0.09	2.58	0.10	4.97	0.19
	500	0.24	0.07	0.19	0.01	3.37	0.14	3.51	0.14	3.29	0.13

Considering the fact that the metals were added in equal mass rather than equimolar amounts, a possible bias is introduced in the comparison of the metals (Gomes et al., 2001). The sorption affinity between the metal cation and the mineral surfaces can therefore be calculated as the amount of each metal present in the adsorption complex, i.e., the share of a given metal in the total amount adsorbed by the soil mineral matrix expressed as percent (%). Table5 presents these values of metal in the adsorption and desorption complexes for each soil.

At the lowest applied concentration (Table 5), the amount of heavy metals adsorbed decreased in order of increasing atomic masses except for Pb. Cr, with the highest molar concentration, occupied 37.94% and 43.11% of the adsorption complex in LAEM and LAAB, respectively. As the concentration increased, competition started to occur and the proportion of Cr, Cu and Pb adsorbed increased compared with Zn and Cd. The percentages of desorbed heavy metals had irregular patterns for both soils. The least desorbed heavy metal from both soils at the various concentrations of mixed solutions added was Cr with 7.83% being the maximum amount desorbed (Table 5). While Cd and Cu had intermediate desorptions, the desorptions of Pb and Zn were the highest from LAEM (Fig. 1). Zinc however, had the highest percent of desorption from LAAB as depicted in Fig. 2.

Table 4: Adsorbed (Ads) and Desorbed (Des) Metal Concentrations (mg/g) for LAEM and LAAB

Metal	Concentration Added (mg/L)	Soil			
		LAEM		LAAB	
		Ads	Des	Ads	Des
Cd	100	0.03	0.027	0.02	0.017
	200	0.02	0.014	0.04	0.042
	300	0.03	0.030	0.06	0.059
	400	0.09	0.084	0.05	0.052
	500	0.18	0.163	0.08	0.074
Total		0.34	0.318	0.25	0.245
Cr	100	0.61	0.012	0.65	0.002
	200	0.69	0.007	0.57	0.006
	300	0.68	0.009	0.76	0.007
	400	0.69	0.012	0.79	0.002
	500	0.87	0.017	0.71	0.008
Total		3.53	0.056	3.49	0.020
Pb	100	0.44	0.028	0.41	0.021
	200	0.70	0.048	0.61	0.048
	300	1.09	0.093	1.36	0.049
	400	1.34	0.242	1.37	0.091
	500	1.55	0.213	1.08	0.135
Total		5.12	0.625	4.82	0.340
Cu	100	0.36	0.033	0.31	0.013
	200	1.17	0.045	1.20	0.059
	300	1.05	0.060	1.31	0.071
	400	1.78	0.105	1.79	0.097
	500	1.48	0.177	0.59	0.140
Total		5.84	0.418	5.20	0.380

Zn	100	0.16	0.052	0.13	0.040
	200	0.07	0.030	0.11	0.068
	300	0.12	0.095	0.17	0.124
	400	0.80	0.249	0.72	0.188
	500	0.33	0.221	0.24	0.132
Total		1.48	0.647	1.37	0.550

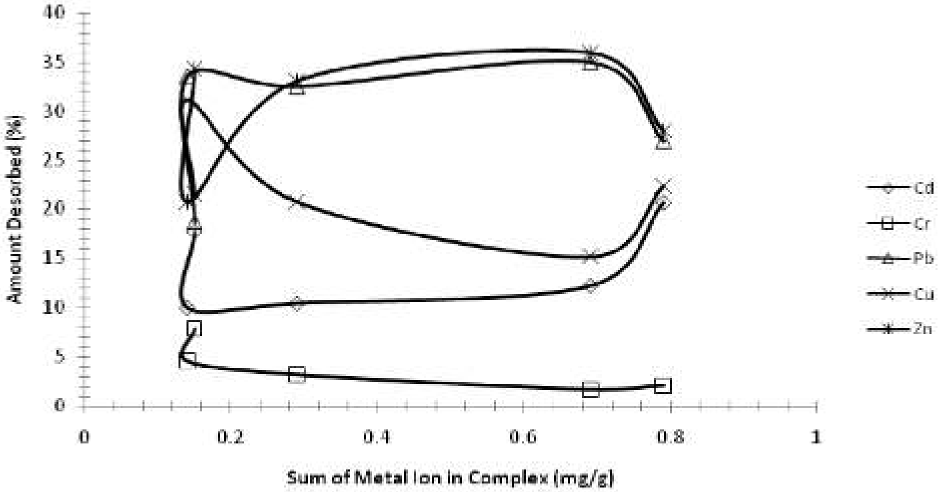

Fig. 1:Percentage of Heavy Metal Cation Desorbed from LAEM as related to the Sum of Metal Cations in the Adsorption Complex.

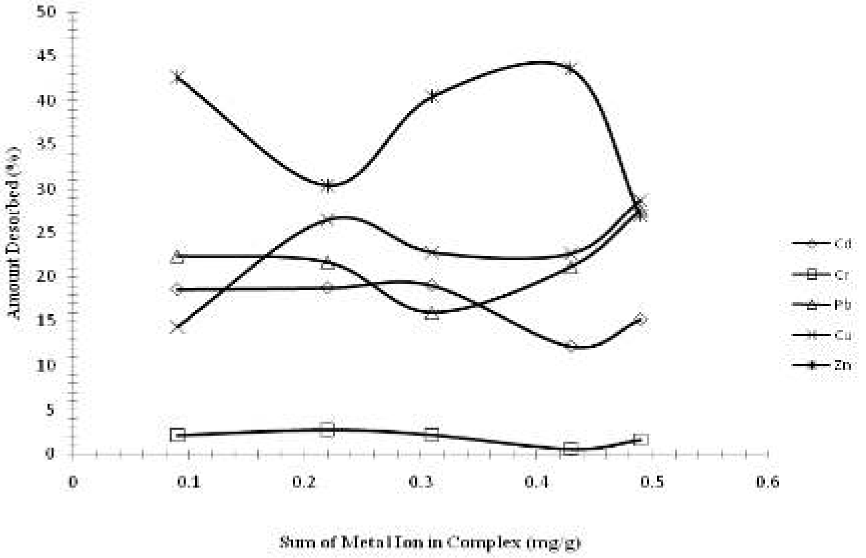

Fig. 2: Percentage of Heavy Metal Cation Desorbed from LAAB as related to the Sum of Metal Cations in the Adsorption Complex

Figs. 3 and 4 show total amounts of all metals adsorbed and desorbed by each of the laterites. Adsorption increased sharply compared with desorption which was gradual at the various concentrations of mixed cations added until added solution has a concentration of 400mg/L. After this concentration, a sharp decline was observed in adsorption. This implied that the laterites may not be easily regenerated for reuse in heavy metal remediation. While desorption was relatively constant with increase in concentration of added metal cations in the case of LAAB, a sharp rise was observed with LAEM. Decrease in sorption after initial increase was in line with the studies of Vega et al. (2006).

Tables 6 summaries the results from correlations between Langmuir and Freundlich isotherms with adsorption and desorption studies. The competitive adsorptions of the heavy metals on LAEM fitted well into the Freundlich isotherm model with the correlations in the range 0.56 – 1.00 while LAAB had 60% fitting into the Langmuir isotherm model with correlations in the range 0.66 – 0.98. The adsorption intensity, n (g/L), and capacity, K_F (mg/g) for LAEM was of the order Cr > Cu >Pb> Zn > Cd. For LAAB, the maximum adsorption equilibrium constant, q_m (mg/g), was highest for Pb followed by Cr, Cu, Zn and Cd in that order which was similar to the observations of Vega *et al.* (2006). These values suggest ease of displacement of Zn and Cd relative to Cr, Pb and Cu. In the desorption studies, the best isotherm model was the Langmuir model. Correlations for Pb and Cr were highest in LAEM and LAAB, respectively. The isotherm models for both adsorption and desorption studies however, generally had poor correlations.

Table 5: Sum of the Metal Cation Adsorbed/Desorbed (mg/Kg) and Percentage of each Metal Cation Adsorbed/Desorbed in the Adsorption Complex

Soils	Sum of Metal Adsorbed (mg/g)	Metal Cations (%)				
		Cd	Cr	Pb	Cu	Zn
ADSORPTION						
LAEM	1.60	1.72	37.94	27.72	22.40	10.23
	2.64	0.57	26.02	26.47	44.39	2.56
	2.97	1.09	22.78	36.65	35.44	4.04
	4.70	1.83	14.74	28.53	37.85	17.06
	4.40	3.98	19.68	35.27	33.65	7.42
LAAB	1.52	1.15	43.11	26.75	20.37	8.63
	2.54	1.68	22.57	24.16	47.45	4.14
	3.65	1.64	20.85	37.08	35.71	4.72
	4.72	1.11	16.73	28.89	37.94	15.32
	2.70	2.78	26.34	40.09	21.90	8.89
DESORPTION						
LAEM	0.15	17.68	7.83	18.69	21.47	34.34
	0.14	9.93	4.57	33.61	31.19	20.70
	0.29	10.40	3.21	32.52	20.74	33.12
	0.69	12.19	1.70	34.97	15.16	35.99
	0.79	20.63	2.13	26.92	22.34	27.96
LAAB	0.09	18.57	2.11	22.36	14.35	42.62
	0.22	18.72	2.75	21.65	26.46	30.42
	0.31	19.01	2.15	15.95	22.78	40.42
	0.43	12.15	0.52	21.13	22.62	43.57
	0.49	15.19	1.56	27.58	28.74	26.93

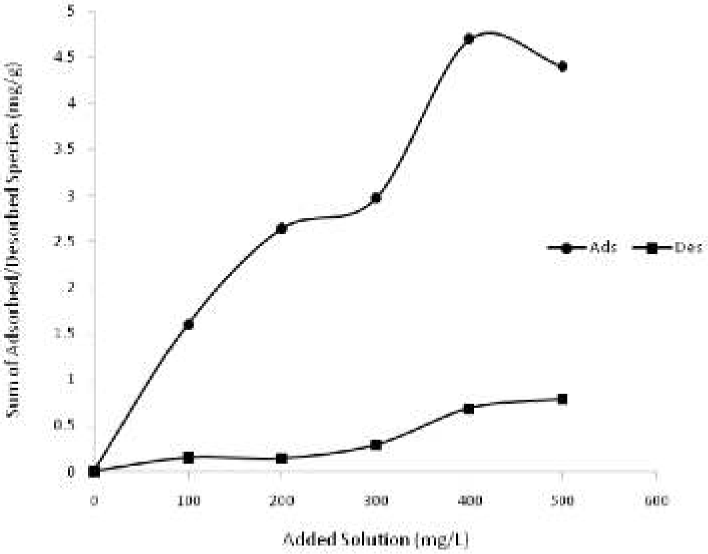

Fig. 3: Comparative Study of the Adsorption and Desorption of All Heavy Metal Species by LAEM.

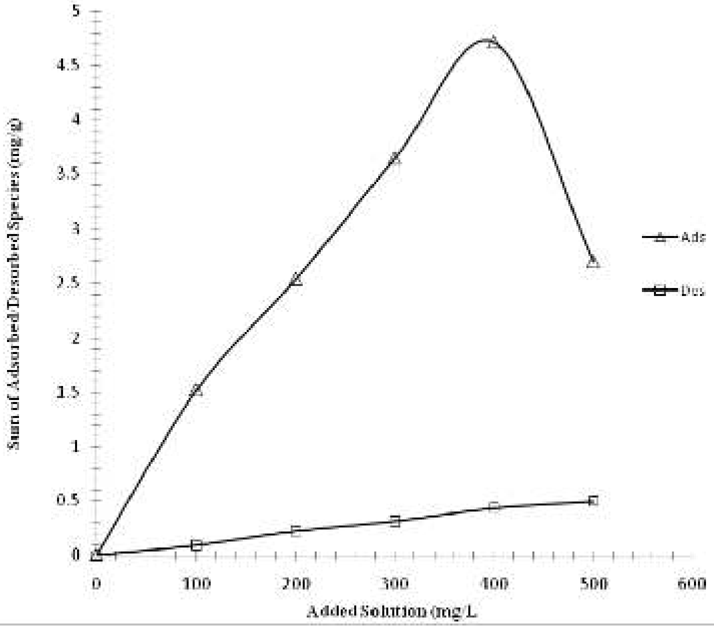

Fig. 4: Comparative Study of the Adsorption and Desorption of All Heavy Metal Species by LAAB

Table 6: Langmuir and Freundlich Isotherm Parameters for Competitive Adsorption on LAEM and LAAB

Soil	Metal	Langmuir			Freundlich			Best-Fitting Model
		K_L (mg/g)	q_m (mg/g)	R^2	K_F (mg/g)	n (g/L)	R^2	
ADSORPTION								
LAEM	Cd	-0.001	-0.098	0.12	7.87×10^{-05}	0.871	0.56	Freundlich
	Cr	0.03	0.846	0.95	0.402	9.267	0.62	Langmuir
	Pb	0.002	3.420	0.84	0.025	1.406	0.98	Freundlich
	Cu	0.003	2.885	0.40	0.037	1.505	0.58	Freundlich
	Zn	2.4×10^{-4}	2.975	0.00	0.010	1.000	1.00	Freundlich
LAAB	Cd	0.001	0.204	0.41	4.3×10^{-4}	1.194	0.90	Freundlich
	Cr	0.067	0.764	0.98	0.491	14.970	0.26	Langmuir
	Pb	0.007	1.675	0.66	0.038	1.644	0.65	Langmuir
	Cu	-0.028	0.622	0.76	0.290	4.568	0.06	Langmuir
	Zn	0.003	0.500	0.18	0.006	1.541	0.31	Freundlich
DESORPTION								
LAEM	Cd	-6.813	5×10^{-4}	0.829	4×10^{-4}	-0.820	0.676	Langmuir
	Cr	8.660	0.976	0.765	0.867	5.631	0.227	Langmuir
	Pb	0.592	1.548	0.936	0.547	2.067	0.898	Langmuir
	Cu	0.359	2.408	0.403	0.638	1.442	0.536	Freundlich
	Zn	0.124	0.477	0.820	0.043	1.209	0.389	Langmuir
LAAB	Cd	-0.036	0.026	2×10^{-4}	8×10^{-4}	1.763	0.149	Freundlich
	Cr	-575.880	0.668	0.927	0.635	-27.174	0.032	Langmuir
	Pb	0.969	1.396	0.654	0.655	1.844	0.520	Langmuir
	Cu	-1.901	0.538	0.587	0.654	2.186	0.309	Langmuir

Data in Tables 5 show that relatively large amount of each of Cr, Cu and Pb were adsorbed compared with Zn and Cd. Due to isotherm irregularity caused by competition among the heavy metals and poor correlation with the Langmuir and Freundlich equations, further analysis of the data was based on the distribution coefficient, K_d (Gomes et al., 2001). High values of $K_d$indicate that a metal has been retained by the solid phase through sorption reactions, while low values of $K_d$indicate that a large fraction of the metal remains in solution (Anderson & Christensen, 1988). $K_d$values are therefore indices of metal mobility and retention (Antoniadis &Tsadilas, 2007). From Table 7 it can be seen that adsorption of Cu, Pb and Cr presented the highest $K_d$values for both soils similar to the observations of Gomes et al. (2001) and Vega et al. (2006). These showed that they were the cations most retained and in general, Cu was strongly retained than Cr and Pb which exchanged positions for LAEM and LAAB. The metals with the lowest $K_d$values were Zn and Cd, showing that, when in competition, they were easily exchanged and substituted by Cu, Pb and Cr. This reasoning is in line with the findings of Gomes et al. (2001) and Vega et al. (2006) and was confirmed by the results of the desorption studies (Table 7) in which Cr, Pb and Cu were strongly retained on the soil while Zn and Cd were easily desorbed. For the two soils Cr however, was strongly retained than Pb and Cu. The adsorption sequences obtained were Cu >Pb> Cr > Zn > Cd and Cu > Cr >Pb$\gg$ Zn > Cd for LAEM and LAAB, respectively, while the sequences which suggested retention in the desorption experiments were Cr > Cu >Pb> Zn > Cd and Cr $\gg$Cu >Pb> Zn > Cd, respectively. The results (adsorption and desorption) strongly suggest that soil loading of Cd and Zn appeared to be of environmental concern than Cu, Cr and Pb.

Table 7: Distribution Coefficients of Metal Ions between Soil and Soil Solution (K_d(L / kg)) after Adsorption / Desorption and Selectivity Sequences

Soil	Metals					Selectivity Sequence
	Cd	Cr	Pb	Cu	Zn	
DSORPTION						
LAEM	0.28	15.5	7.99	5.59	1.96	
	0.08	5.21	5.38	14.20	0.35	
	0.11	2.92	5.71	5.41	0.42	
	0.22	2.09	5.04	8.00	2.51	
	0.36	2.09	4.49	4.20	0.70	
Total	1.05	27.80	28.60	37.40	5.93	Cu >Pb> Cr > Zn > Cd
LAAB	0.18	18.9	6.82	4.47	1.5	
	0.22	4.01	4.42	15.10	0.55	
	0.20	3.40	8.24	7.70	0.61	
	0.13	2.46	5.18	8.12	2.21	
	0.15	1.66	2.76	1.34	0.50	
Total	0.88	30.40	27.40	36.70	5.38	Cu > Cr >Pb» Zn > Cd
ESORPTION						
LAEM	0.82	49960.00	14600.00	9975.06	2131.47	
	3.56	104223.50	13560.00	25309.31	1279.22	
	6.93	72395.83	10662.55	16676.65	260.61	
	6.00	57820.00	4547.08	15976.12	2222.89	
	147.50	50296.51	6279.01	7362.42	475.29	
Total	164.81	334695.90	49648.63	75299.55	6369.48	Cr > Cu >Pb> Zn > Cd
LAAB	0.56	332336.00	18509.91	22160.00	2302.38	
	0.85	92031.25	11649.21	19323.90	542.37	
	1.51	113300.00	26422.62	17487.50	387.62	
	0.69	348137.50	14009.34	17411.34	2859.30	
	3.33	92592.11	7030.42	3211.54	823.71	
Total	6.93	978396.90	77621.48	79594.27	6915.37	Cr » Cu >Pb> Zn > Cd

Conclusion

The laterites from Emuhu, Delta State (LAEM) and Abeokuta, Ogun State (LAAB) were acidic, low in organic matter and CEC with the consequences of being non-supportive of vegetation. The trends of adsorption observed for the two laterite samples were the same. The trends of desorption of metal cation were Cr < Cd < Cu <Pb< Zn and Cr < Cd <Pb< Cu < Zn for LAEM and LAAB, respectively. For adsorption, as the concentration of metal cation in mixed solution increased, the proportion of Cr, Cu and Pb adsorbed by the soils increased compared with Zn and Cd. For the desorption counterpart however, irregular patterns were observed for both soils. The competitive adsorptions of the heavy metals on LAEM fitted well into the Freundlich isotherm model while LAAB had 60% fitting into the Langmuir isotherm model. The adsorption intensity suggested ease of displacement of Zn and Cd relative to Cr, Pb and Cu from adsorbent. In the desorption studies, the best isotherm model was the Langmuir model with Pb and Cr being highly favoured in terms of adsorption. $K_d$values which are indices of metal mobility and retention gave adsorption sequences being Cu>Pb> Cr > Zn

> Cd and Cu > Cr >Pb≫ Zn > Cd for LAEM and LAAB, respectively, while the sequences which suggest retention in the desorption experiments were Cr > Cu >Pb> Zn > Cd and Cr ≫ Cu >Pb> Zn > Cd for LAEM and LAAB, respectively. In immobilizing mixed cations in soils, laterite will serve in the retaining Cr, Pb and Cu better than Zn and Cd. LAEM however, has better potentials than LAAB.

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