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*Experimental*

# SORPTION OF COMPETING HEAVY METALS ON 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 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. Laterite affinities for heavy metal adsorption 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. 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 Emuhu Laterite, LAEM and Abeokuta Laterite, LAAB, can receive and hold Cr, Pb and Cu pollutants in solution. They can thus be recommended for remediation of the three metals from industrial waste effluents.

**Key Words**: Competition, isotherms, remediation, selectivity, soils, toxicity

## 1.0 INTRODUCTION

Many anthropogenic activities such as industrial wastewater discharge, agricultural fertilizers, and mining leaching, introduce heavy metals into the water body (Huang et al., 2019). These metal ions are of concern to public health and the environment if inappropriately discharged (Laus, Costa, Szpoganicz & Favere, 2010) because they are bio-accumulative and may enter into the human food chain with consequential health difficulties. The potential sources of heavy metal ions in wastewaters are diverse (Tekin & Acikel, 2023). 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. A number of deficiencies are associated with conventional methods of treatment including but not limited to high operational costs, excessive sludge yields to be disposed-off, and poor usability (Bhatnagar & Silanpaa, 2010). For economy, effectiveness and reduction of the deficiencies of conventional methods for the removal of metals from wastewaters, new separation methods are developed. Adsorption as a treatment process, has attracted considerable interest and appears to be the most widely used. 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 abundant, cheap, and widely available and are environmentally friendly (Montalescot et al., 2015). Naturally occuring materials therefore, are of interest with agricultural products that have no food value being the most prominent (Bayuo, Rwiza, Sillanpaa & Mtei, 2023). Despite the over-whelming advocacy and use of the agricultural wastes as adsorbents, they are not without disadvantages. The adsorption capacities of untreated agricultural wastes are low, their chemical oxygen demand, biochemical oxygen demand and total organic carbon are high (Nakajima & Sakaguchi, 1990). Plant wastes require modification for suitability in the removal of heavy metals.

Laterite is 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. Fe and/or Al like-containing natural materials such as raw laterite, siderite and hematite, are getting pronounced these days. A naturally occurring and abundant clay, raw laterite, is been studied widely (Maiti, Basu, & De, 2012).

Being a naturally abundant, cheap, and environmentally friendly material, its suitability for use for heavy metal remediation cannot be overemphasised. From literature search, adsorption studies using laterite have involved single-component metal ions simulated wastewater. Industrial wastewater effluents however, are multicomponent systems with competing metal ions. The objective of this study therefore, was to evaluate competitive adsorption of Cd, Cr, Pb, Cu and Zn ions from two laterite samples obtained from Nigeria.

## 2.0 MATERIALS AND METHODS

### Laterite Sampling and Pre-treatment

Laterite was obtained in the month of November from the non-vegetative region (30-50cm) of a laterite site at 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 using a soil auger. They were separately collected in polythene bags and labelled for ease of identification as LAAB and LAEM, to represent laterite from Abeokuta and Emuhu, respectively. The laterite samples were dried for 72 h, ground and screened with a 1.0 mm mesh and stored for analysis.

### Soil Physicochemical Parameters

The methods of Rice, Baird, and Eaton (2017) and Sparks et al. (1996) were used to determine the physicochemical properties of laterite samples. Laterite pH and electrical conductivity (EC) were determined using 40% soil suspension in deionised water with a Jenway 3540 pH-Conductivity meter. The micro Kjeldahl method was used for total nitrogen (TN) content of soils determination. The ascorbic acid method was used for soil phosphorus content determination at 885 nm using UV-visible spectrophotometer (Jenway, 6300). Acid ammonium fluoride extraction method was used for the determination of laterite extractable phosphorus (P). Ammonium acetate (pH 7) was used to measure exchangeable cations (K, Na, Ca and Mg). K and Na were determined using flame atomic emission method. Complexometric titration using EDTA was used for laterite exchangeable Ca and Mg determination. Particle size distribution determination was done by the hydrometer method. The metal oxides were determined using X–ray Fluorescence Spectrometer Model ARL-9900, OASIS at 40kV, 30mA.

### Competitive Adsorption

The method of Bassam et al. (2022) was used for the adsorption capacities of the laterite samples determination. The results of experiments were used for the calculation of each metal adsorption distribution coefficients in each soil using

Eqn 1:

$$\boldsymbol{K_d = \frac{q_e}{C_e}} \qquad (1)$$

$K_d$ = the Distribution Coefficient,

$q_e$ = amount of metal adsorbed by laterite (mg/g)

$C_e$ = the amount of metal unadsorbed in solution at equilibrium (mg/L).

Sorption data were characterised 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 Eqn 2.

$$\boldsymbol{\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{Kq_m}} \qquad (2)$$

Where $q_e$ is the amount of metal adsorbed by laterite (mg/g),

$q_m$ = the maximum adsorption capacity of adsorbent (mg/g),

$K$ = the equilibrium constant of Langmuir Isotherm (mg/g),

$C_e$ = 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 Eqn 3

$$log\, q_e = log\, K_F + 1/n\, log\, C_e \qquad (3)$$

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

All determinations were done in duplicates. The mean values of all determinations and all other statistical analyses were performed using SigmaPlot 14 (Systat Inc).

## 3.0 RESULTS AND DISCUSSION

The results of the physicochemical analyses of laterite samples are presented in Table 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. Both soils had a ΔpH ($pH_{KCL} - pH_{H2O}$) value of -0.7. This implied that both soils slight negative charge at the equilibrium pH (Cazanga et al., 2008). This suggested that $H^+$ on the soils were replaced by metal ions in solution. Soil pH affects heavy metals availability in soil. When pH is around 6.5 – 7, metal ions are relatively unavailable in solution. Precipitation of metal elements will increase due to the formation of hydroxides, carbonates and organic complexes thereby reducing mobility (Antoniadis, Tsadilas & Ashworth, 2007). 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 $1.5 \times 10^{-3}$% 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%.

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

The equilibrium concentrations, Ec, and the quantity of metal cations adsorbed in the supernatant after adsorption experiment are presented in Table 2. Both soils followed a general trend. Cr, Pb and Cu showed relatively low Ec at the concentrations of application. The implication was a higher soil surface affinity by the metals Cr, Pb and Cu 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 attributed to the type of metal-surface interaction (Qasem, Mohammed, & Lawal, 2021). The retention of Zn and Cd is more of covalent bonding with the laterite structures. Similar results were obtained by Gomes et al. (2001), that concurrent competition usually favour Cr, Pb and Cu, in soils than Zn, Cd and Ni.

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 (Table 3) mineral matrix expressed as percent.

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 | $1.5 \times 10^{-3}$ |
| 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

Table 2: Equilibrium concentration (Ec (mg/L)) and adsorbed metal cation (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 |
| | **Total** | | **0.34** | | **3.53** | | **5.12** | | **5.84** | | **1.48** |
| **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 |
| | **Total** | | **0.25** | | **3.49** | | **4.82** | | **5.20** | | **1.37** |

Table 3: Sum and percentage metal cation adsorbed 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 |

At 100 mg/L, the amount of metals ion sorbed decreased in order of increasing atomic masses except for Pb. Cr, occupying 37.94% and 43.11% of the adsorption complex in LAEM and LAAB, respectively. Increase in concentration led to increase in competition, with the amount of Cr, Cu and Pb adsorbed higher compared with Cd and Zn. Adsorption increased sharply at the various concentrations of mixed cations added up to 400mg/L. Thereafter, a sharp decline was observed in adsorption. Decrease in sorption after initial increase was in line with the studies of Vega, Covelo, and Andrade (2006). Tables 4 summarises the results of the Langmuir and Freundlich isotherms as related to the adsorption studies. The competitive adsorptions of 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.

Tables 5 shows that relatively large amount of Cr, Cu and Pb were adsorbed compared with Zn and Cd. The use of distribution coefficient, $K_d$ is necessitated by the irregular isotherms due to heavy metals competition and poor fitting with the Langmuir and Freundlich equations, (Gomes et al., 2001). The higher the $K_d$ value, the stronger the sorption of the metal to the solid phase while the lower the $K_d$ value, the larger the fraction of metal ions in solution (Anderson & Christensen, 1988). $K_d$ values are therefore indices of metal mobility and retention (Antoniadis & Tsadilas, 2007). Adsorption of Cu, Pb and Cr had the highest values of $K_d$ 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. Zn and Cd had the lowest $K_d$ values with the implication that, Cu, Pb and Cr easily replaced them when competing. This reasoning is in line with the findings of Gomes et al. (2001) and Vega et al. (2006). 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. The results strongly suggest that sorption of Cd and Zn onto the laterite samples will be of concern than Cu, Cr and Pb.

Table 4 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** | | | | | | | | |
| | Cd | -0.001 | -0.098 | 0.12 | $7.87 \times 10^{-05}$ | 0.871 | 0.56 | Freundlich |
| **LAEM** | | | | | | | | |
| | 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 | $2.4 \times 10^{-4}$ | 2.975 | 0.00 | 0.010 | 1.000 | 1.00 | Freundlich |
| | Cd | | | | | | | Freundlich |
| **LAAB** | | 0.001 | 0.204 | 0.41 | $4.3 \times 10^{-4}$ | 1.194 | 0.90 | |
| | 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 |

Table 5 Metal ions distribution coefficients after adsorption and selectivity sequences

| **Soil** | **Metals** | | | | | **Selectivity Sequence** |
|---|---|---|---|---|---|---|
| | Cd | Cr | Pb | Cu | Zn | |
| **ADSORPTION** | | | | | | |
| **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 |

## 4.0 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. As the concentration of metal cation in mixed solution increased, the proportion of Cr, Cu and Pb adsorbed by the soils increased relative to Zn and Cd. 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. $K_d$ 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. In immobilising 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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