Full Paper

INFLUENCE OF pH AND METAL CONCENTRATION ON CU ADSORPTION BY TWO SOILS OF CONTRASTING FEATURE

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ABSTRACT

The influence of soil pH and soil copper concentration on the adsorption of the metals by the soil particles was studied in batch conditions. The metal was introduced into the soil through the application of copper based fungicide. Copper adsorption was studied by means of adsorption isotherms using Cu concentrations range of 3.25 g/l to 4.5 g/l and solution pH of 3, 4, 5 and 6. Results indicated that the four solution pH were significantly ($P < 0.05$) different in their effects on the adsorption of the metal to the two soils. The two soils are also significantly different in their adsorption capacity. The adsorbed copper increased with increase in solution pH and copper concentration with the maximum adsorption occurring at pH of 6 and copper concentration of 4.00 g/l. However, concentrations 4.25 g/l and 4.50 g/l were not significantly different in their effects on the amount of copper adsorbed by the two soils. The amount of copper adsorbed per unit mass of the soil on the average increased from 15.25mg/g at pH 3 to 26.13 mg/g at pH 6 while it increased on the average from 19.20 mg/g at copper concentration of 3.25 g/l to 21.30 mg/g at copper concentration of 4.50g/l. Regression analysis revealed a strong correlation between adsorbed copper and solution pH within individual copper concentrations. From the isotherm analysis, sorption of copper to the two soil types considered was best described by Langmuir equation.

Keywords: *Kocide 101, Adsorption isotherm, equilibrium concentration, solution pH*

1. INTRODUCTION

Land application of fertilizers and pesticides in agriculture has contributed to a continuous accumulation of heavy metals in soils (Adriano, 1986; Sarkar, 2002; Krumholz *et al.*, 2003). The behaviour of metals in soil is governed largely by sorption and desorption reactions with different soil constituents (Singh *et al.*, 2001). The adsorption of chemicals to sediments and soils is an important process that affects a chemical's distribution in the environment. If a chemical is adsorbed to soil particles, it will remain on the soil surface and will not reach ground water. If a chemical is not adsorbed, it will leach through the soil profile and may reach ground waters and the surface waters thereby contaminating them. Availability of trace elements to plants is affected by a variety of factors including soil solution pH, soil texture, and soil moisture, temperature, oxide content, carbonate content, organic matter content, and clay mineralogy (Goldberg *et al.*, 2005).

The total soluble copper in acid soils is found as organic matter complexes (Sposito, 1989; Baker, 1993). Thus the copper availability for plants depends on its characteristics of adsorption (Raghupathi and Vasuki, 1993). Copper is a very common substance that occurs naturally in the environment and spreads through the environment through natural phenomena. Copper can be released into the environment by both natural sources and human activities. Examples of natural sources are wind-blown dust, decaying vegetation, forest fires and sea spray. A few examples of human activities that contribute to copper release into the environment include mining, metal production, wood production, application of copper fungicides and phosphate fertilizer production. Because copper is released both naturally and through human activity, it is spread widely in the environment. Most copper compounds will settle and be bound to either water sediment or soil particles. Soluble copper compounds which form the largest threat to human health usually occur in the environment after release through application in agriculture.

Copper enters agricultural ecosystems through applications of copper – containing fungicides, stable manures, and liquid or solid wastes from copper related mining and manufacturing. When copper is released into soil, it can become strongly attached to the organic material and other components (e.g., clay, sand, etc.) in the top layers of soil and may not move very far when it is released. When copper and copper compounds are released into water, the copper that dissolves can be carried in surface waters either in the form of copper compounds or as free copper or, more likely, copper bound to particles suspended in the water. Even though copper binds strongly to suspended particles and sediments, it is possible to suggest that some water-soluble copper compounds do enter groundwater.

Soil sorption studies are commonly performed to evaluate the extent of solute retention by a soil or soil constituents. Different soils possess different capacity to adsorb metals. Sorption studies are often used in an attempt to generate the equilibrium distribution coefficient (K_d), the ratio of metal sorbed to soil in solution at equilibrium which may be utilized in transport models. Sorption studies are also used for the comparison of the relative retention of several metals by a soil or the relative retention of a metal by several soils and are used in correlation studies to determine the relative importance of a soil's chemical and physical properties for metal retention (McLean and Bledsoe, 1992). Sorption studies also can be used to evaluate the effect that changing a soil solution parameter, e.g., adjusting of pH has on metal retention by a soil. All soil minerals are capable of adsorbing Cu ions from solution and these properties depend on the surface charge carried by the adsorbents. The surface charge is strongly controlled by pH; therefore, the adsorption of Cu ion can be presented as a function of pH (Kabata-Pendias, 2000). Spathariotis and Kallianou (2001) reported that the percentage of copper, zinc and cadmium adsorbed as a function of pH increased in sigmoidal form. The interactions of metals with humic acids extracted from marine sediments (Rashid, 1971) and soils (Kerndorff and Schnitzer, 1980) have been reported. Metal adsorption capacity changes with pH, concentration and type of metal. In order to express the adsorption behaviour of metals to soil particles, sorption isotherms which describe equilibrium sorption are commonly used. The most widely employed are those proposed by Langmuir and Freundlich. A sorption isotherm is the relationship between the amount of metal sorbed and the equilibrium concentration of the metal.

Kocide 101 is an inorganic copper-based fungicide whose active ingredient is cupric hydroxide (77%) and inert ingredient (23%). The chemical name of this fungicide is copper hydroxide (cupric hydroxide) with chemical formula of CuH_2O_2 $(Cu\ (OH)_2)$ .The metallic copper equivalent of the fungicide is 50% and it is commonly used by farmers in Nigeria to control fungi infection on beans, carrot, coffee, tomatoes, pepper and potatoes etc. It is a blue powder, which is hardly soluble in water. It is compatible with most other pesticides.

The main objectives of the study were therefore to quantify the adsorption of copper by two soil series of contrasting features from Southwestern Nigeria and to examine the influence of solution pH on the adsorption of the metal to soil particles. Adsorption isotherms were measured and modeled to see the correlation between copper adsorption and the pH. Sorption coefficients were also determined for copper in the two soils as influenced by the solution pH.

2. MATERIALS AND METHODS

The two soil types used in this work were common agricultural soils in Ile – Ife, southwestern Nigeria. The soils were collected from surface 0 – 15cm on a 5 – 10 year natural bush fallow plots from two sites in the area. The total annual rainfall of the study area is about 1350 mm. The average daily minimum temperature ranged between 20^{O}C and 22^{O}C, and the average maximum temperature between 27^{O}C and 35^{O}C. The two soils are classified at series level as *Apomu* and *Egbeda* series (*Ojanuga*, 1975). The physico – chemical properties of the two soils are summarized in Table 1.

The adsorption experiment was carried out by means of a batch sorption test (Ozanne and Shaw, 1967; Gray *et al.*, 1998) at room temperature (28 ± 1^{O}C). Copper (II) solutions were prepared in 0.01M $CaCl_2$ using cupric hydroxide (*Kocide 101*). Air-dried soil sample of about 1g was equilibrated with 10 ml solution containing the desired concentrations of the copper fungicide in a centrifuge. The effect of the initial concentration of the metal in the background solution of 0.01M $CaCl_2$ (varied between 3.25 g/l and 4.5 g/l) and the influence of the pH (3, 4, 5 and 6) were studied in order to determine their effects on the removal of copper ions from the solution. The pH values were measured with a pH meter. The pH was varied using 0.1mol.md^{-3} HCl or 0.1mol.dm^{-3} NaOH. During the experiments the amount of soil (1g) and the stirring speed of the centrifuge (400rpm) were kept constant. The tubes containing the soil and fungicide solution were shaken for 3 hours. After equilibration and centrifugation, the supernatant was removed and taken to the laboratory for analysis for copper using Atomic Absorption Spectrophotometer. Adsorption was estimated from the decrease in concentration of the metal in the fungicide in the liquid phase after equilibration according to the formulas:

$$C_S = \frac{C_O - C_W}{(W/V)} \tag{1}$$

Where C_s is the amount adsorbed $(\mu g/g)$, C_O is the initial concentration $(\mu g/ml)$, C_W is the final concentration in the solution $(\mu g/ml)$, W is the weight of the soil (g) and V is the solution volume (ml)

3. ANALYSIS OF DATA

3.1. Sorption Isotherms of copper

The experimental data on equilibrium sorption of copper by the two soils in six different initial solution concentrations and four levels of pH were subjected to analysis by means of the three commonly used sorption isotherm models, namely the Linear (McLaren and Cameron, 1990), Langmuir and Freundlich models (Wu, 1989; Atanassova, 1995; Atanassova and Okazaki, 1997)

The Linear isotherm model is:

$$C_S = a + K_d C_W \tag{2}$$

The Langmuir isotherm model is:

$$\frac{C_W}{C_S} = \frac{1}{kb} + \frac{C_W}{b} \tag{3}$$

The Freundlich isotherm model is:

$$Log.C_S = LogK_d + \left(\frac{1}{n}\right) LogC_W \tag{4}$$

where *a* is a constant which corresponds to the intercept on the C_s versus C_W plot, b is the maximum sorption capacity of the soil and k is the coefficient related to bonding energy. K_d is the adsorption coefficient in cm^3/g. $\left(\frac{1}{n}\right)$ is a constant that depends on the pollutant (in this case the trace metal) and b the maximum adsorption.

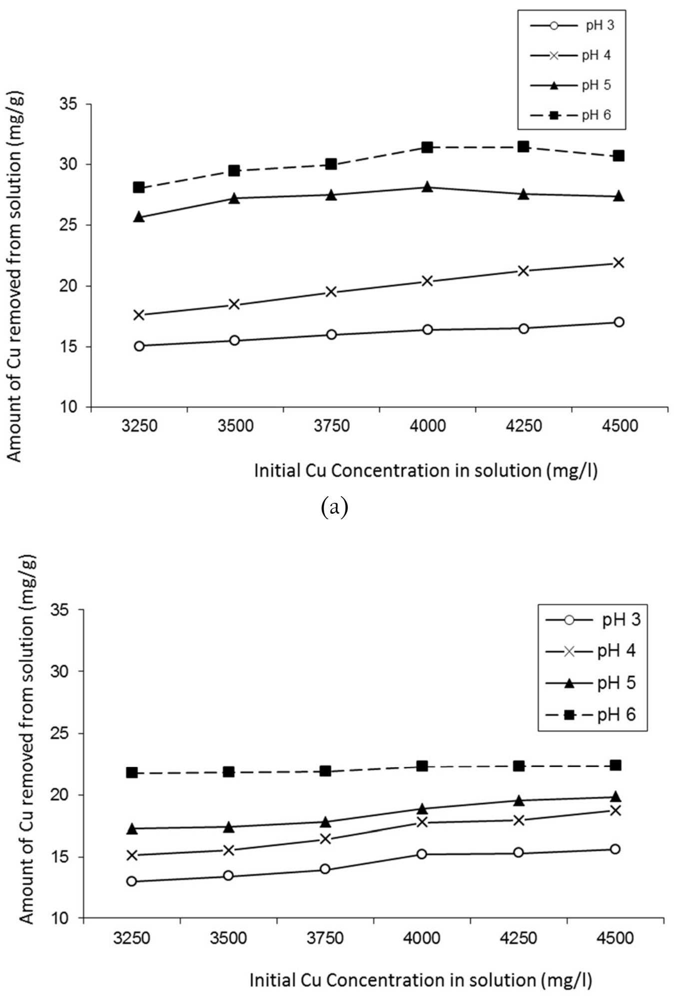
3.2. Sorption Isotherm

4.1.1 Equilibrium concentration and Amount of Copper Adsorbed

The sorption affinity of copper varied substantially with the solution pH, initial copper concentration in the solution and the soil types. In a two component system (sorbent and solution) a graph of copper concentration in the solid phase Cu_{ads} (mg/g) plotted as a function of copper concentration in the liquid phase Cu_{eq} (mg/l) at equilibrium is shown in Figure 1. The correlation coefficients derived from the plots for the two soil samples are higher than 0.95 for Langmuir model and 0.85 for Freundlich model. The Langmuir model provides the parameters of the maximum adsorption (b) and a constant related to bonding-energy of the adsorbate to the adsorbent (K) while Freundlich equations provide rough measurement of the adsorption intensity (1/n) and adsorption capacity (K_f) of the adsorbent. Table 3 lists all the adsorption parameters of b, K (for Langmuir equation), a and K_d (for Linear equation); K_f, and 1/n (for Freundlich equation) and their correlation coefficients, r^2.

Table 1: Some selected Physico – Chemical Properties of the soils

Soil series	Organic matter content (%)	CEC (cmol/kg)	Particle size distribution			Textural classification	Taxonomy
			Sand (%)	Silt (%)	Clay (%)		
Apomu	1.16	6.75	82.5	7.0	10.5	Loamy sand	Alfisols
Egbeda	1.85	10.12	68.0	10.0	22.0	Sandy clay loam	Inceptisols



(a)

(b)

Figure 1: Effects of initial concentration on Cu removed from Kocide 101 solution per gram of soil (a) Egbeda soil and (b) Apomu soil as a function of solution pH

4. RESULTS AND DISCUSSION

The amount of copper adsorbed increased with the equilibrium copper concentration to a maximum value. This is typical of Langmuir type of Isotherms (Goldberg and Criscenti, 2008) and the results were in agreement with previous reports (Padmanabham, 1983; Wu, 1989; Atanassova, 1995; Wang et al., 1995; Atanassova and Okazaki, 1997; Yu et al., 2002). This is also evident from r^2 values (0.91 – 0.99) for the two soils at the four different solution pH considered (Table 3) for Langmuir Isotherm as against the r^2 ranges for the other two equations. Therefore, Langmuir equation is better for the adsorption properties of copper (II) ions to the two soil types considered in this study and thus should be used. The maximum adsorption of copper to the soil particles occurred at the pH of 6 for the two soil types. At this high pH, the ion is likely to be specifically adsorbed in the soil surface and may be bonded by covalent linkages.

4.1.2. Equilibrium concentration and initial copper concentration

The effect of initial copper concentration in the fungicide solution on the equilibrium concentration is shown in Table 2. For all the four pH considered in this work, the equilibrium copper concentration in the solution increases with the increase in the initial copper concentration in the solution for the two soils. The concentration of copper in the solution at equilibrium increases by 60.4 %, 55.4%, 156.9% and 224.9% for pH of 3, 4, 5 and 6, respectively, as the initial copper concentration increases from 3.25 *g/l* to 4.50 *g/l* for Egbeda soil. However the increases in the equilibrium copper concentrations reduced to 50.8%, 51.3%, 65.2%, and 110.7% for pH of 3, 4, 5 and 6, respectively, for Apomu series. This is because soils with high clay content and high organic matter content have a higher capacity to adsorbed chemicals (Riise and Salbu, 1992). Apomu series which contains a higher portion of sand shows lower sorption capacity for all the four pH considered.

Egbeda adsorbed more copper than Apomu series. At maximum initial concentration (4.5 *g/l*) of copper in the solution, 37.8 %, 48.6%, 60.9% and 68.2% of copper in the solution of Kocide 101 at the pH of 3, 4, 5 and 6, respectively, were adsorbed by Egbeda while 34.6%, 41.6%, 44.1% and 49.8% of copper were adsorbed by Apomu soil at the four different pH, respectively. However, the amount of copper adsorbed by Egbeda at solution pH 5 and 6 was not significant ($P < 0.05$). At these two solution pH, increasing the initial copper concentration in the solution did not affect the amount of copper adsorbed by the soil. Also for Apomu, the amount of copper adsorbed at solution pH of 6 was not significant ($P < 0.05$). However, the remaining three solution pH significantly affected the amount of copper adsorbed by this soil at the six initial concentration of copper in the solution. At solution pH of 6 (like for Egbeda soil), increasing the initial copper concentration in the solution did not affect the amount of copper adsorbed by the soil. This may be due to the fact that at this pH the adsorption capacity of the soil was low and additional input of the metal into the soil solution will not affect the amount of the metal adsorbed

The relationships between the amount of copper adsorbed and the initial copper concentration in the solution at the four solution pH are presented in Table 4. The regression between amount of copper adsorbed and initial copper concentration in the solution when done across all the four solution pH gave poor relationships for both Egbeda and Apomu soils (r^2 =0.03 and 0.09, respectively). However, the relationship within each solution pH was strong (except for the pH of 5) with r^2 values of 0.98, 0.99, 0.44, 0.71 for Egbeda soil and r^2 values of 0.94, 0.97, 0.95, and 0.89 for Apomu soil.

It is interesting to note that at lowest initial concentration (3.25 g/l) considered, it was observed that the amount of copper adsorbed by the two soils as a function of the initial copper concentration is higher than at the high initial copper concentration in the solution. At

Table 2: Equilibrium concentration of Cu as affected by solution pH and initial copper concentration

Soil series	pH	Initial Cu concentration in the fungicide solution (*g/l*)					
		3.25	3.5	3.75	4.0	4.25	4.5
Apomu	3	1.95 (0.01)[a]	2.16 (0.01)	2.35 (0.00)	2.40 (0.01)	2.72 (0.02)	2.94 (0.01)
	4	1.74 (0.01)	1.95 (0.01)	2.11(0.01)	2.22 (0.02)	2.46 (0.01)	2.63 (0.01)
	5	1.52 (0.01)	1.76 (0.01)	1.97 (0.01)	2.11 (0.01)	2.30 (0.01)	2.52 (0.01)
	6	1.07 (0.01)	1.32 (0.01)	1.56 (0.01)	1.77 (0.01)	2.02 (0.01)	2.26 (0.01)
Egbeda	3	1.75 (0.01)	1.95 (0.01)	2.15 (0.01)	2.36 (0.01)	2.60 (0.02)	2.80 (0.02)
	4	1.49 (0.02)	1.66 (0.01)	1.80 (0.01)	1.97 (0.02)	2.13 (0.02)	2.31 (0.01)
	5	0.69 (0.11)	0.78 (0.01)	1.00 (0.01)	1.19 (0.01)	1.49 (0.01)	1.76 (0.01)
	6	0.44 (0.01)	0.55 (0.01)	0.75 (0.01)	0.86 (0.02)	1.11 (0.01)	1.43 (0.01)

[a] *Standard deviation values are in bracket*

Table 3: Linear, Langmuir and Freundlich sorption isotherms constants based on batch equilibrium data of Copper in solution at the four solution pH

	Egbeda Solution pH				Apomu Solution pH			
	3	4	5	6	3	4	5	6
No of observations (Initial Conc.)	6	6	6	6	6	6	6	6
Linear isotherm constant								
a	12.05	9.69	25.99	28.00	7.49	7.65	12.44	21.11
K_d	0.0018	0.0054	0.0011	0.0025	0.0028	0.0042	0.003	0.0006
R^2	0.97	0.99	0.30	0.53	0.90	0.93	0.92	0.88
Langmuir isotherm constants								
K	0.0014	0.001	0.026	0.020	0.001	0.0004	0.0011	0.014
b (ml/mg)	21.37	40.16	28.33	32.26	27.62	37.17	27.25	23.09
R^2	0.99	0.99	0.99	0.99	0.93	0.91	0.97	0.99
Freundlich isotherm constants								
K_f	»100	2.09	17.33	17.12	2.76	3.44	1.72	16.59
1/n	5.67	0.49	0.06	0.08	0.47	0.52	0.31	0.04
R^2	0.68	0.99	0.55	0.71	0.89	0.93	0.87	0.74

Table 4: Relationships between adsorbed copper (mg/g) and initial copper concentration in the solution

Soil Type	Solution pH	Regression equation
Egbeda	3	$Cu_{ADS} = 0.0015Cu_{IC} + 10.213$ ($r^2 = 0.98^*$) n = 6
	4	$Cu_{ADS} = 0.0035Cu_{IC} + 6.308$ ($r^2 = 0.99^*$) n = 6
	5	$Cu_{ADS} = 0.0123Cu_{IC} + 22.609$ ($r^2 = 0.44^{NS}$) n = 6
	6	$Cu_{ADS} = 0.0023Cu_{IC} + 21.289$ ($r^2 = 0.71^{NS}$) n = 6
	Overall	$Cu_{ADS} = 0.002Cu_{IC} + 15.11$ ($r^2 = 0.03^{NS}$) (n = 24)
Apomu	3	$Cu_{ADS} = 0.0023Cu_{IC} + 5.662$ ($r^2 = 0.94^*$) n = 6
	4	$Cu_{ADS} = 0.003Cu_{IC} + 5.193$ ($r^2 = 0.97^*$) n = 6
	5	$Cu_{ADS} = 0.0023u_{IC} + 9.466$ ($r^2 = 0.95^*$) n = 6
	6	$Cu_{ADS} = 0.001Cu_{IC} + 19.909$ ($r^2 = 0.89^{NS}$) n = 6
	Overall	$Cu_{ADS} = 0.002Cu_{IC} + 10.06$ ($r^2 = 0.09^{NS}$) (n = 24)

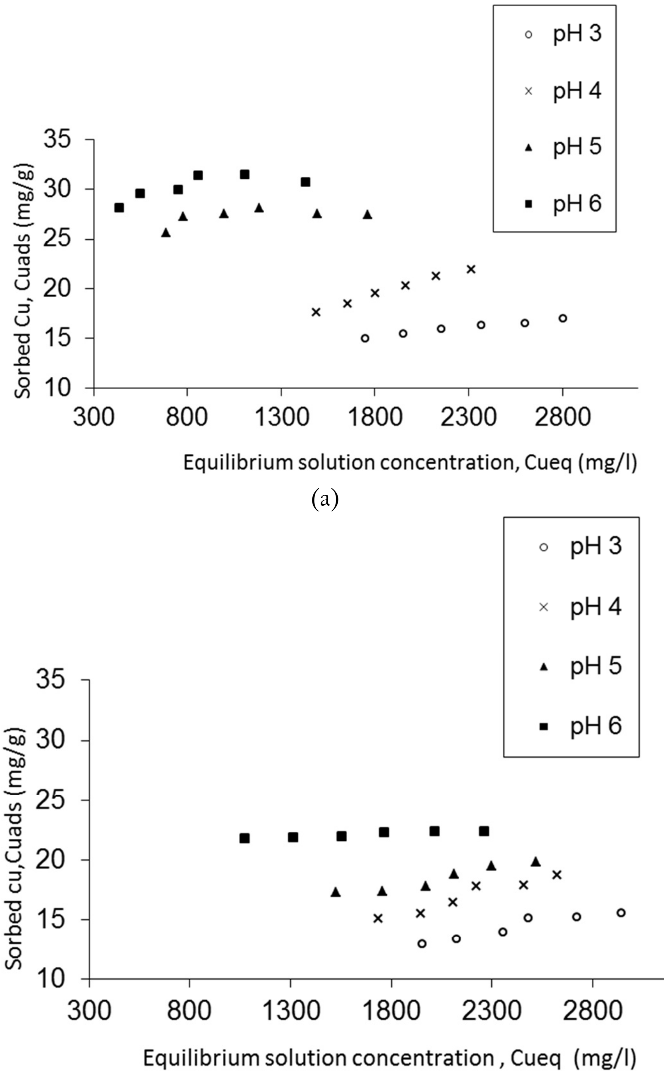
Cu_{ADS}, adsorbed Copper (mg/g);
Cu_{IC}, initial Copper concentration in the solution (mg/l);
*significant at 5% probability level;
NS not significant

the low initial copper concentration in the solution, 46.3 %, 54.2 %, 78.9 % and 86.4 % of the metal in the solution at the pH of 3, 4, 5, and 6, respectively, were adsorbed by Egbeda soil while 40 %, 46.6 %, 53.1 % and 70 % of the metal were adsorbed by Apomu soil at the four different pH at the low initial metal concentration in the solution. This is due to the fact that at low concentration, the metal added to the soil through the fungicide was below the adsorption capacity of the soils which is more dependent on the soil cation exchange capacity, Organic matter content and other physical and chemical properties of the soils. According to Mohamed et al. (1994), at low concentration, clay particles tend to disperse due to the full development of the diffuse double layer, therefore clay particle surfaces were in contact with solution at the maximum.

4.1. Effects of factors on copper adsorption

4.2.1 Effect of pH on the adsorption of copper

The interactive effect of soil types and pH on copper adsorption is shown in Figure 2. Each data is a mean of the six initial copper concentration considered. The pH of the solution was significant ($P < 0.05$) in its effects on the adsorption of copper to the two soils under consideration. The amount of copper adsorbed per unit mass of the soil on the average when the two soils were considered together increased from 15.24 mg/g when the solution pH was 3 to 26.13 mg/g when the pH was 6. The effect of pH was more pronounced in Egbeda soil than in Apomu soil. It is noteworthy here that relative higher copper was adsorbed by Egbeda soil as the solution pH changes from 3 to 4. This result was similar to what was reported by Schmuhl et al. (2001) that the most effective pH for Cu (II) removal was at pH range from 3 to 5. The increase in the amount of copper adsorbed by Apomu soil as the solution pH increases was relatively steady with the exception of solution pH of 6. However, relative higher copper was adsorbed by Apomu soil as the solution pH changes from 5 to 6.



(b)

Figure 2: Isotherm for the adsorption of Copper ions from Kocide 101 solution onto soil at different pH(a) Egbeda soil and (b) Apomu soil

The relationships between the amount of copper adsorbed and the solution pH at the six different initial copper concentrations are presented in Table 5. The regression between amount of copper adsorbed and solution pH is stronger in Egbeda (r^2 =0.94) than in Apomu. (r^2 =0.87). Also, the relationship within each initial copper concentration in the solution was very strong with r^2 values not less than 0.94 for Egbeda soil and 0.95 for Apomu soil. The strong relationship observed when regression is done across all the six initial copper concentration considered in this work implies that the soil solution pH is one of the factors controlling the adsorption of copper to soil particles.

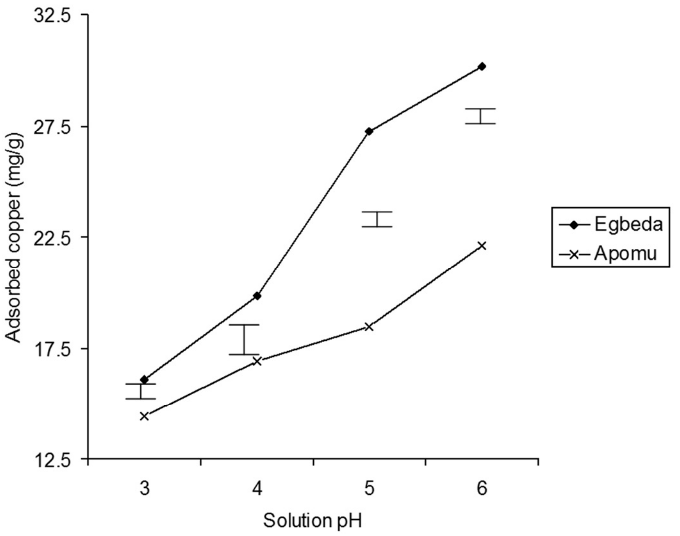


Figure 3 : Effect of solution pH and soil types on the amount of copper adsorbed (mg/g). The vertical bars represent Least Significant Difference (LSD) at 0.05.

Table 5: Relationships between adsorbed copper (mg/g) and solution pH

Soil Type	Initial conc. (*mg/l*)	Regression equation
Egbeda	3250	$Cu_{ADS} = 4.715\,pH + 0.385$ ($r^2 = 0.95^*$) (n = 4)
	3500	$Cu_{ADS} = 5.078\,pH - 0.191$ ($r^2 = 0.94^*$) (n = 4)
	3750	$Cu_{ADS} = 4.995pH + 0.76$ ($r^2 = 0.96^*$) (n = 4)
	4000	$Cu_{ADS} = 5.287pH + 0.261$ ($r^2 = 0.97^*$) (n = 4)
	4250	$Cu_{ADS} = 5.101\,pH + 1.233$ ($r^2 = 0.95^*$) (n = 4)
	4500	$Cu_{ADS} = 4.651\,pH + 3.308$ ($r^2 = 0.99^*$) (n = 4)
	Overall	$Cu_{ADS} = 4.9712pH + 0.959$ ($r^2 = 0.94^{**}$) (n =24)
Apomu	3250	$Cu_{ADS} = 2.843\,pH + 3.999$ ($r^2 = 0.96^*$) (n = 4)
	3500	$Cu_{ADS} = 2.717\,pH + 4.826$ ($r^2 = 0.95^*$) (n = 4)
	3750	$Cu_{ADS} = 2.525pH + 6.16$ ($r^2 = 0.96^*$) (n = 4)
	4000	$Cu_{ADS} = 2.244pH + 8.442$ ($r^2 = 0.96^*$) (n = 4)
	4250	$Cu_{ADS} = 2.273\,pH + 8.539$ ($r^2 = 0.99^*$) (n = 4)
	4500	$Cu_{ADS} = 2.153\,pH + 9.444$ ($r^2 = 0.97^*$) (n = 4)
	Overall	$Cu_{ADS} = 2.4592pH + 6.902$ ($r^2 = 0.87^{**}$) (n =24)

Cu_{ADS} , adsorbed Copper (mg/g); pH, solution pH;

*significant at 5% probability level;

** significant at 1% probability level.

4.2.2. Effect of initial copper concentration on adsorption of copper

The initial copper concentration in the solution was also significant ($P < 0.05$) in its effects on the adsorption of copper to the two soils under consideration. Figure 4 shows the interactive effect of soil types and copper concentration on the adsorbed copper. The amount of Copper adsorbed was highest when the initial Copper concentration in the solution was 4.00 g/*l* (a mean of 21.69 mg/g) and lowest when the initial Copper concentration in the solution was 3.25 g/*l* (a mean of 19.20 mg/g). As the level of copper ion in the solution increases from 3.25 g/*l* to 4.50 g/*l*, the amount adsorbed also increases. At copper concentration of 4.00 g/l, monolayer capacity corresponding to complete surface coverage is likely to be reached and adsorption beyond this point is likely to be a surface precipitation or condensation of multi-layers. According to Duncan's multiple range tests, initial Copper concentrations of 3.25, 3.50 and 3.75 g/*l* were significantly different in their effect on the amount of Copper adsorbed at 5 % probability level. Initial Copper concentrations of 4.00 and 4.25 g/*l* were not significantly different as well as initial concentrations of 4.25 and 4.50 g/*l* ($P < 0.05$).

4.2.3. Effect of soil type on adsorption of copper

The influence of soil type on the amount of copper adsorbed to soil particles is shown in Figure 5. The two soil types were significantly different in their effect on the adsorption of Cu ($p < 0.05$). On the average, 17.97 mg/g of copper was adsorbed by Apomu series while 23.33 mg/g of the same metal was absorbed by Egbeda. This is expected because of the higher clay content and cation exchange capacity of Egbeda soil (Table 1).

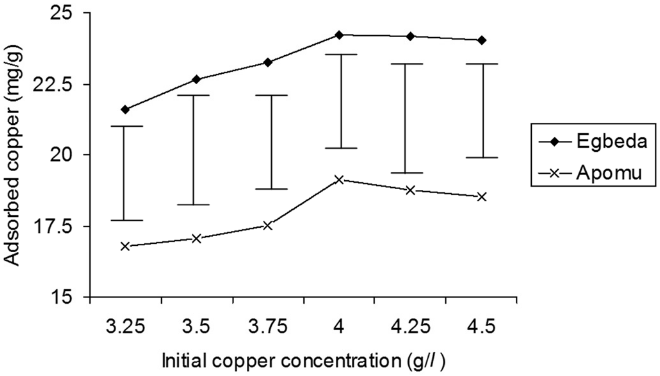


Figure 4 : Effect of soil types and initial copper concentration on the amount of copper adsorbed (mg/g) by the two soils. The vertical bars represent Least Significant Difference (LSD) at 0.05

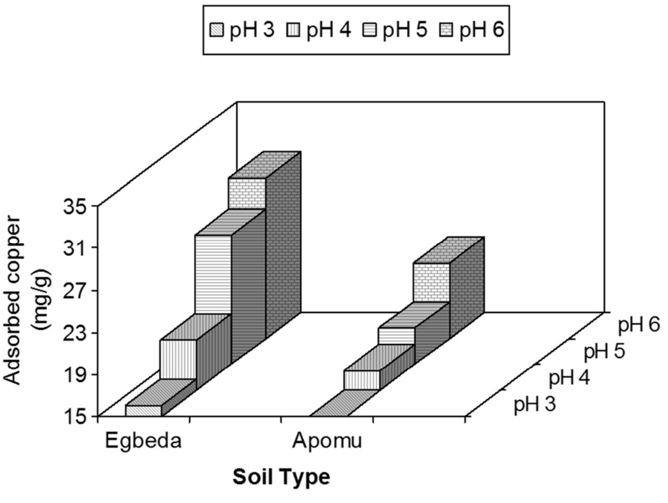


Figure 5 Effect of soil type on adsorbed copper

The regression equations between the equilibrium concentration and adsorbed copper for the different solution pH considered in this work based on Langmuir model (the model that best described the relationship) are presented in Table 6. The regression between amount of copper adsorbed and the concentration of Copper in equilibrium when done across all the solution pH gave a strong relationship (R^2= 0.91) with Egbeda soil and relatively strong relationship (R^2= 0.73) with Apomu. However, the relationship within each solution pH was very strong and positive with R^2 value of 0.99 each for the four levels of solution pH for Egbeda soil and values 0.93, 0.91, 0.97 and 0.99 for solution pH 3, 4, 5 and 6, respectively, for Apomu. The strong relationship observed within the solution pH and when regression was done across all the four solution pH considered in this work implies that the equilibrium concentration of Copper in the solution is the major determining factor controlling the amount of Copper to be adsorbed to soil particles.

Table 6: Relationships between adsorbed Copper (mg/g) and equilibrium Copper concentration in the solution.

Soil Type	Solution pH	Regression equation
Egbeda	3	$Cu_{ADS} = Cu_{EQ}/(0.0468Cu_{EQ} + 34.304)$ $(r^2 = 0.99^{**})$ n = 6
	4	$Cu_{ADS} = Cu_{EQ}/(0.0249Cu_{EQ} + 47.894)$ $(r^2 = 0.99^{**})$ n = 6
	5	$Cu_{ADS} = Cu_{EQ}/(0.0353Cu_{EQ} + 1.379)$ $(r^2 = 0.99^{**})$ n = 6
	6	$Cu_{ADS} = Cu_{EQ}/(0.031Cu_{EQ} + 1.523)$ $(r^2 = 0.99^{**})$ n = 6
	Overall	$Cu_{ADS} = Cu_{EQ}/(0.067Cu_{EQ} - 26.72)$ $(r^2 = 0.91^{**})$ $(n = 24)$
Apomu	3	$Cu_{ADS} = Cu_{EQ}/(0.0362Cu_{EQ} + 80.121)$ $(r^2 = 0.93^{**})$ n = 6
	4	$Cu_{ADS} = Cu_{EQ}/(0.0269Cu_{EQ} + 69.707)$ $(r^2 = 0.91^{**})$ n = 6
	5	$Cu_{ADS} = Cu_{EQ}/(0.0367Cu_{EQ} + 34.987)$ $(r^2 = 0.97^{**})$ n = 6
	6	$Cu_{ADS} = Cu_{EQ}/(0.043Cu_{EQ} + 3.138)$ $(r^2 = 0.99^{**})$ n = 6
	Overall	$Cu_{ADS} = Cu_{EQ}/(0.070Cu_{EQ} - 24.69)$ $(r^2 = 0.73^{*})$ $(n = 24)$

Cu_{ADS}, adsorbed Copper (mg/g); Cu_{EQ}, concentration of Copper in equilibrium (mg/l);
*significant at 5% probability level;
**significant at 1% probability level.

5. CONCLUSIONS

The equilibrium concentration of copper in soil solution increased with increase in the initial copper concentration and decreased with the solution pH. Sorption of copper to the two soil types considered in this work may be explained by all the three sorption isotherms tested with Langmuir equation fitting the data better than the other two isotherms. There appeared to be a strong correlation between sorption and equilibrium copper concentration in the solution ($r^2 > 0.90$). The adsorption process of copper to the two soils seems to be solution pH driven than the initial copper concentration in the solution. The effect of pH was more pronounced in Egbeda than in Apomu series. The most effective pH range for the removal of copper by the Apomu was between 4 and 5 while the range was between 3 and 4 for Egbeda soil. As the level of copper ion in the solution increases from 3.25 g/l to 4.50 g/l, the amount adsorbed also increases with maximum adsorption occurring at copper concentration of 4.00 g/l. A monolayer capacity corresponding to complete surface coverage is reached at copper ion concentration of 4.00g/l.

REFERENCES

Adriano, D.C. Trace Elements in Terrestrial Environments. New Yort: Springer-Verlug, 533p, 1986

Atanassova, I.D. Adsorption and desorption of Cu at high equilibrium concentrations by soil and clay samples from Bulgaria. Environ. Pollut. 87:17 – 21, 1995.

Atanassova, I.D. and Okazaki, M. Adsorption – desorption characteristics of high levels of copper in soil clay fractions. Water Air Soil Pollut. 98:213 – 228, 1997.

Baker, D.E. Copper. In: ALLOWAY, B.J.ed. Heavy metal in soils. Glasgow: Blackie Academic & Professional, pp 151 -176, 1993.

Gray, C.W.; McLaren, R.G.; Roberts, A.H.C. and Condron, I.M. Sorption and desorption of cadmium from some New Zealand soils: effect of pH and contact time. Australian Journal of Soil Research, *36, 199 – 216,* 1998.

Goldberg, S and Criscenti, L.J. Modeling Adsorption of Metals and Metalloids by soil components. In: Biophysico-Chemical Processes of Heavy Metals and Metalloids in Soil Environment. Edited by Antomio, V., Pan Ming, H and Geoffrey, M.G. John Wiley & Sons Inc., 215 – 263, 2008.

Goldberg, S.; Lessch, S.M. and Suarez, D.L. Predicting Trace Element Adsorption by soil using Soil Chemical Parameters. In: Proceedings of the International Salinity Forum, Managing Saline Soils and Water: Science, Technology, and Soil Issues. April 25-27, 2005. Riverside, CA pp. 197 – 200, 2005.

Kabata-Pendias, A. Trace Elements in Soils and Plants. CRC Press London, 106 -291, 2000.

Kerndorff, H. and Schnitzer, M. Sorption of metals on humic acid. Geoch. Et Cosm. Acta, vol. 44, 1701 – 1708, 1980.

Krumholz, L.R.; Elias, D.A. and Safita, J.M. Immobilization of cobalt by sulfite-reducing bacteria in subsurface sediments. Geomicrobiol J., 20:61 – 72, 2003.

McLaren, R.G. and Cameron, K.C. Soil Science, an introduction to the properties and management of New Zealand soils, 1990.

McLean, J.E and Bledsoe, B.E. Behaviour of Metals in Soils. Ground Water Issue. US EPA. EPA/540/S – 92/018, 1992.

Mohamed, A.M.O.; Young, R.N.; Tan, B.K.; Farkas, A. and Curtis, L.W. Geoenvironmental assessment of a micaceous soil for its potential use as an engineered clay barrier. Geotechnical Testing Journal, ASTM, 17 (3): 291 – 304, 1994.

Ojanuga, A.G. Morphology, Physical and Chemical Characteristics of Ife and Ondo areas. Nigerian Journal of Soil Sci., 9, 225 – 269, 1975.

Padmanabham, M. Adsorption – Desorption behaviour of copper (II) at the goethite – solution interface. Aust. Journal Soil Res. 21:309 – 320, 1983.

Raghupathi, H.B. and Vasuki, N. Copper adsorption of some soils of North Karnataka. Jour. Ind. Soc. Soil Sci., v.41, pp 70 – 74, 1993.

Rashid, M.A. Role of humic acids of marine origin and their different weight fractions in complexing di- and tr-valent metals. Soil Sci., vol. 111, 298 – 306, 1971.

Riise, G. and Salbu, B. Mobility of dichlorprop in the soil water system as a function of different environmental factors I. A batch experiment. The science of the Total Environment. 123/124, 399 – 409, 1992.

Sarkar, B. Heavy metals in the Environment. New York: Marcel Dekker., 344p, 2002.

Schmuhl, R.,; Krieg, H.M. and Keizer, K. Adsorption of Cu (II) and Cr (VI) ions by chitosan: Kinetics and equilibrium studies. Water SA, 27 (1), 1 – 8, 2001.

Singh, S.P.; Ma, L.Q. and Harris, W.G. Heavy metal interactions with phosphatic clay: sorption and desorption behaviour. Journal of Environ. Qual 30:1961 – 1968, 2001.

Spathariotis, E. and Kallianou, C. Adsorption of copper, zinc, and cadmium on clay fraction of two acid soils: Surface complexation modeling. Commun. Soil Sci., plant Analysis 32 (19 & 20), 3185 – 3205, 2001.

Sposito, G. The chemistry of soils. New York: Oxford University Press. 69pp, 1989.

Ozanne,P.G. and Shaw , T.C. Phosphate sorption by soil as a measure of phosphate requirement for pasture. Australian Journal of Agricultural Research, 18, 601 – 612, 1967.

Wang, W.; Shao, Z. and He, Q. Study on adsorption affinities of Co, Cu, Pb and Zn for different red soil clays. Acta Pedologica Sinica, 32: 167 – 178, 1995.

Wu, M. Study on the specific adsorption of copper ion by soils and its characteristics. Acta Pedologica Sinica, 26: 31 – 41, 1989.

Yu, S.; He, Z.L.; Huang, C.Y.; Chen, G.C. and Calvert, D.V. Adsorption – Desorption Behavior of Copper at contaminated levels in red soils from China. Journ. Of Environmental Quality 31:1129 – 1136, 2002.