

Effect of contact time on adsorption of copper on soils of dissimilar lithologies in acid soils of South-eastern Nigeria

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Abstract

The effect of contact time on the adsorption of copper on soils of different parent material in acid soils of southeastern Nigeria was observed. The parent materials and locations were Olivine basalt (Ikom), shale underlay by false bedded sand stone (Ishiagu) and coastal plain sands (Ihiagwa). Result showed that at 30 minutes, percent copper adsorption on soils of Ikom, Ihiagwa and Ishiagu were 92.9 %, 92.3 % and 93.2 % respectively. While at 240 minutes, percent copper adsorption on soils of Ikom, Ihiagwa and Ishiagu were 93.8 %, 92 % and 93 % respectively. There was no significant difference on percent copper adsorption with time on the three parent materials. The distribution coefficient (K_d) was highest at 180 min. (665.6 mL/g) in Ikom and lowest at 30 mins. (300.5 mL/g) in Ihiagwa. A non-significant positive correlation ($p \leq 0.05$) was found between adsorption and silt, organic matter, clay, pH and CEC ($r = 0.21, 0.14, 0.10, 0.15$ and 0.16) respectively. While adsorption correlated negatively with sand ($r = 0.17, p \leq 0.05$). Soil pH, organic matter content, cation exchange capacity (CEC), clay and silt content were the important soil properties influencing adsorption of copper on the studied soils. The presence of montmorillonite and other 2:1 clay minerals on soils of Ikom and Ishiagu give then the potential of being a better sink for contaminant like copper, lead in the environment. They can hold, adsorb or retain low molecular mass organic acids, which increase their adsorptive capacity for contaminant like copper, cadmium, lead etc. The information on these soils as well as the properties of these soils should be considered in disposal of Cu-containing materials.

Keywords: Adsorption and affinity of copper, contact time, lithology, acid soils, south-eastern Nigeria.

Introduction

Heavy metals such as lead and copper have great ecological importance due to their toxicity and

accumulative behavior. Metals of particular toxic significance are cadmium (Cd), copper (Cu), lead (Pb), zinc (Zn), and chromium (Cr). The contamination of soil with various heavy metal ions is a major problem which has

received attention in recent times (Jiang et al., 2008; Abdu and Mohammed, 2016; Azeez et al., 2018). As trace elements some heavy metals like zinc and copper are essential to maintain metabolism of humans, animals and plant life. However at higher concentrations they lead to serious poisoning. The presence of toxic metals in the environment may lead to bioaccumulation, geoaccumulation and biomagnifications (Abida et al. 2008).

Copper can be introduced into the soil environment through both pedogenic and anthropogenic process (Schulin et al., 2007). Copper is largely retained in the soil, thus its mobility increases with the decrease of pH (Schulin et al., 2007).

Adsorption of metal is higher in strongly acidic soils (typical of most tropical soils) which are usually rich in (crystalline and amorphous) oxides and hydroxides of iron anaaluminium (Kuo 1990).

Adsorption and desorption therefore can be affected by many factors such as pH and time (Stahl and James, 1991), cation exchange capacity, insoluble organic matter and clay content (Mc Bride and Blasaik 1979), competition from other ions (Covelo et al., 2004). Studies on adsorption of heavy metals onto soil and clay minerals showed that metal ion concentration and soil type affected the adsorption of heavy metal onto soils and clay minerals (Qin et al., 2004; Adebowale et al., 2005). The most important chemical process affecting heavy metal behavior and bioavailability in soil is metals adsorption from solution phase onto solid phase (Alloway, 1990; Bradl, 2004). Studies on Pb (II) adsorption onto clay minerals and oxides showed that soil type, ionic strength, ion type, contact time affected the adsorption of heavy metals onto soil and clay minerals (Lee et al., 1998; Sipos et al., 2005; Adebowale, et al., 2006; Wang et al., 2009).

The adverse effect of heavy metals is related to the ability of the soil to adsorb these elements. Such information is essential and is needed in order to predict the environmental impact of copper from anthropogenic sources as well as to develop necessary measure to regulate the usage and disposal of copper containing materials on agricultural soils. Although extensive researches on adsorption have been carried out on temperate soils, there is paucity of data on both adsorption and desorption reactions on tropical and subtropical soils (Naidu et al., 1997). Although adsorption process is widely applied, it is still only partially understood (Unuabonah et al., 2007). Studies have shown that increase in contact time favour adsorption of metal ions because the sorbed phase of metals transformed from loosely bound phase to

strongly bounded phase as contact time increases (Lim et al., 2002 ; Qin et al., 2004). However there are few studies and limited information on the effect of contact time on adsorption and affinity of copper onto acid soils.

This paper investigated the impact of contact time on adsorption and affinity of copper onto acid soils, with the aim to provide scientific information that will help manage copper contaminated soils as well as develop regulations on how to use and dispose Cu-containing materials on these agricultural soils.

Materials and Methods

The acid soils of selected parent materials at different locations in southeastern Nigeria, Ikom in Cross –River state with olivine basalt as the parent material, Ishiagu in Ebonyi state with shale underlay by false bedded sand stone and Ihiagwa in Imo state with coastal plain sands as the parent material. Ikom lies between latitudes $6^{\circ} 51' N$ and $8^{\circ} 15' E$, Ishiagu lies between $5^{\circ} 57' N$ and $7^{\circ} 34' E$ and Ihiagwa lies between $5^{\circ} 21' N$ and $7^{\circ} 15' E$ (Fig.1). The temperature of the study areas ranged from $26^{\circ} C$ to $29^{\circ} C$. Mean annual rainfall of about 2400 mm. The rainfall pattern is bimodal with peaks in the month of July and September with a short dry spell in the month of August known as August break (Onweremadu, 2007). Soils were of a flat topography (0- 1 percent). The areas have humid tropical climate. People in the study areas engage themselves in different socio-economic activities such as farming and trading. Samples were collected from the three different locations at 0 – 15 cm depth using an auger. Soil samples collected were air dried and sieved using 2 mm mesh sieve and taken to the laboratory for further analysis. The particle size distribution was determined using the hydrometer method (Gee and Or, 2002). Organic carbon was determined using Walkley and Black wet oxidation method (Nelson and Sommers, 1982). Cation exchange capacity (CEC) of the soils was determined by the method of Rhoades in Page et al (1982). Soil pH was determined in water using the pH meter at soil: water ratio of 1:2.5 (Hendershot et al 1993). The background concentration of copper (Cu) of the three locations was determined after digestion of soil samples with a mixture of concentrated $HClO_4$ and HNO_3 at a ratio of 2:1 and copper extracted using 0.5 M HCl (Lacatusu, 2000). The copper concentration in the extractant was determined using Atomic Absorption Spectrophotometer (AAS) (Model AA 500 PG Instrument U.K).

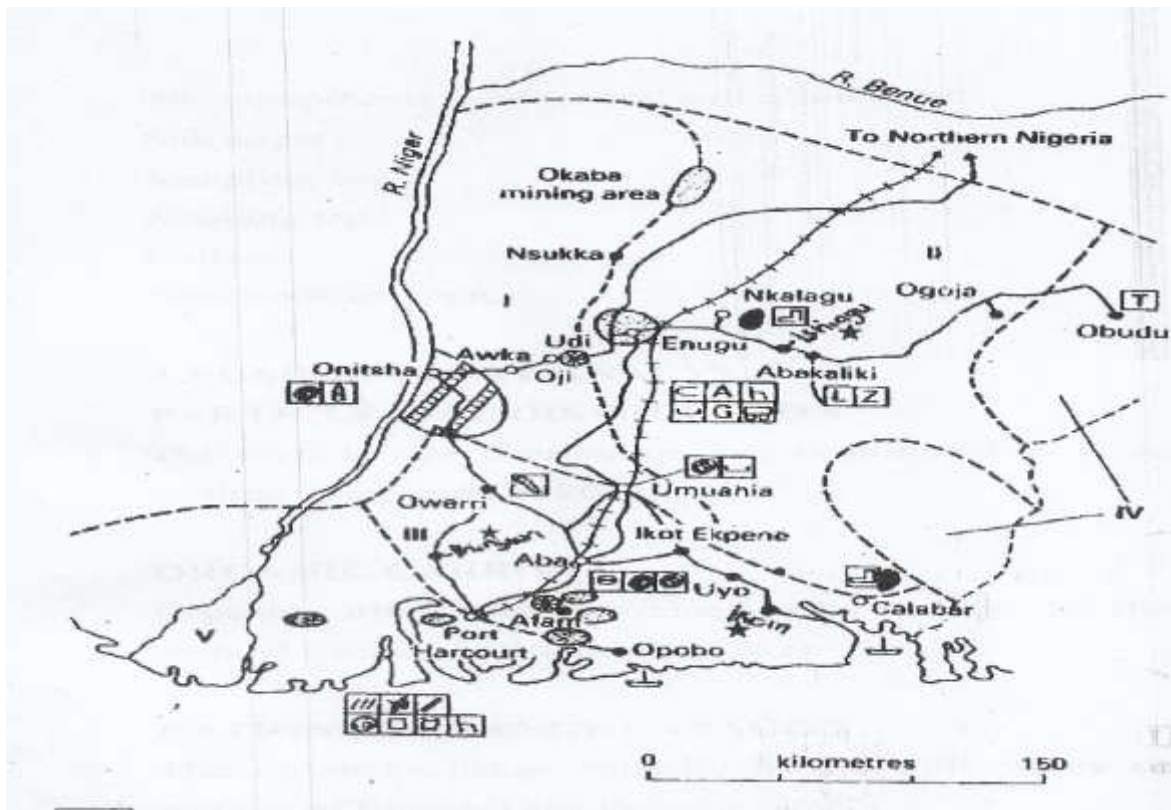


Fig. 1: Map of the study area showing the studied locations

* = studied locations

Adsorption studies

Twenty-five milliliters of background electrolyte KCl in 0.01 mol L⁻¹ containing 100 mg L⁻¹ copper was separately added to 1 g soil. The pH of the solution was adjusted to pH 5.5±0.2. These solutions were agitated in a shaker for 2 h, equilibrated for 22 h and centrifuged at 3900 r/min for 10 min and filtered through a 0.45 µm membrane. The copper concentrations in the filtrates were measured at different time interval 30, 60, 120, 180 and 240 mins. using the atomic absorption spectrophotometer (AAS). The amount of copper adsorbed was calculated by the difference between the total applied copper and the amount of copper remaining in the equilibrium solution.

Copper adsorption was calculated from the equations;

$$\text{Adsorption capacity} = \left(\frac{C_i - C_e}{w}\right)v$$

$$\% \text{ Adsorption} = \frac{C_i - C_e}{C_i} \times 100$$

$$\text{Distribution coefficient (Kd)} = \frac{C_i - C_e}{C_e} \frac{v}{w}$$

Where C_i = initial concentration of copper in soil solution (mg/L), C_e = equilibrium concentration of copper in soil solution (mg/L), V = volume of copper in solution (ml), w = weight of soil (g). The copper used was in the form of Cu(NO₃)₂. The KCl was often used as soil background electrolyte in adsorption study.

Statistical analysis

The experiments were carried out in triplicate and only the mean values are reported. All data were processed using Microsoft excel 2010, SAS version 2008 model and Sigma plot 10. Simple linear correlation analysis was used to show the relationship between adsorption and selected soil properties. Duncan multiple range test was used to detect the significant difference between means of different soils.

Results and Discussion

Soil properties of the studied locations

The results of selected physicochemical properties of the soils of selected parent materials are presented in Table 1. Percent sand ranged from 501.88 g/kg, 741.87 g/kg and 885.2 g/kg for Ikom, Ishiagu and Ihiagwa respectively. The

higher sand particle in the soil of Ihiagwa could be attributed to the nature of parent material which is coastal plain sands. This result agrees with report by Nkwopara et al. (2018) who shows that soil of coastal plain sands have more sand than bentonite. However, there was no significant difference between sand particles of soil of Ihiagwa and Ishiagu, while there was significant difference between the soils of Ihiagwa and Ishiagu and that of Ikom ($p \leq 0.05$). Silt particles ranged from 42.2 g/kg to 225.6 g/kg. Silt content of the soils showed a significant difference ($p \leq 0.05$). This is in line with Nkwopara et al. (2018) who reported that there was significant difference in silt content of coastal plain sands and bentonite. Clay content varied between 65.8 g/kg to 272.5 g/kg. Higher clay content in Ikom could be attributed to the nature of parent material olivine basalt. However, there was no significant difference between clay content of soil of Ihiagwa and Ishiagu, While there was significant difference between the soils of Ihiagwa and Ishiagu and that of Ikom ($p \leq 0.05$). pH in water were 6.35, 5.96 and 7.76 for Ikom, Ihiagwa and Ishiagu respectively. pH in soils of Ikom and Ihiagwa showed no significant difference while there was significant difference between soils of Ikom and Ihiagwa and that of Ishiagu. Organic matters were 65.37 g/kg, 54.07 g/kg and 56.37 g/kg for Ikom, Ihiagwa and Ishiagu respectively. Organic matter in the soils of Ihiagwa and Ishiagu showed no significant difference while there was significant difference between soils of Ihiagwa and Ishiagu and that of Ikom. CEC were 3.89, 2.32 and 2.86 for Ikom, Ihiagwa and Ishiagu respectively. There was significant difference in CEC in all the soils. Low CEC in soils could be attributed to leaching. Similar finding has been reported by Nkwopara et al. (2018) on soils of coastal plain sands. Clay mineralogy of the soil showed that kaolinite and quartz were the dominate minerals however; montmorillonite and other 2:1 clay minerals occurred in Ikom and Ishiagu. This is as a result of the underlain parent material olivine basalt and

shale respectively. The presence of montmorillonite and other 2:1 clay minerals on soils of Ikom and Ishiagu give then the potential of being a better sink for contaminant like copper, lead in the environment. They can hold, adsorb or retain low molecular mass organic acids, which increase their adsorptive capacity for contaminant like copper, cadmium, lead etc. by forming bridging bonds (Huang et al., 2010).

Table 1: Properties of soil at the studied locations

Location	Depth (cm)	Sand (g/kg)	Silt (g/kg)	Clay (g/kg)	pH (H ₂ O)	OC (g/kg)	OM (g/kg)	CEC (cmol/kg)	Clay minerals
Ikom	0-20	525.2	225.6	249.2	6.67	35.5	61.2	3.77	Kaolinite
Ikom	0-20	445.2	225.6	329.2	6.15	39.5	68.1	3.90	quartz, montmorillonite
Ikom	0-20	535.2	225.6	239.2	6.24	38.8	66.8	4.02	Gibbsite
Mean		501.88a	225.6a	272.53a	6.35a	37.93a	65.37a	3.89a	
Ihiagwa	0-20	885.2	35.6	79.2	5.94	31.5	54.3	2.25	Kaolinite, quartz
Ihiagwa	0-20	875.2	45.6	79.2	5.95	30.5	52.6	2.47	
Ihiagwa	0-20	895.2	45.6	59.2	6.01	32.2	55.3	2.25	
Mean		885.2b	42.27b	72.53b	5.96a	31.4b	54.07b	2.32b	
Ishiagu	0-20	745.2	195.6	59.2	7.45	30.9	53.3	2.67	Gibbsite, illite, kaolinite,
Ishiagu	0-20	695.2	225.6	79.2	7.48	32.5	56.0	3.32	vermiculite,
Ishiagu	0-20	785.2	155.6	59.2	8.37	34.7	59.8	2.60	montmorillonite
Mean		741.87b	192.27c	65.86b	7.76b	32.7b	56.37b	2.86c	
LSD (0.05)		52.08	46.89	54.49	0.820	3.128	5.428	0.493	

OC = Organic carbon, OM = Organic matter, CEC = Cation exchange capacity, Clay minerals (Nkwopara et al., 2016)

Effect of time on adsorption

Fig. 2 shows that there was an increase in percent adsorption of copper within 30 to 60 mins and then decreased within 60 mins to 180 mins and increased again within 120- 180 min and decreased within 180 – 240 mins. The equilibrium was not reached within 240 mins. The effect of contact time on adsorption of Cu ion is contrary to previous observation by Nkwopara and Hu (2018) and Adebowale et al. (2006) that adsorption of Pb ion onto variable charged soils and kaolinite increased with time and reached equilibrium after 40mins, 8 mins and 20 mins for variable charge soils, P-modified and unmodified kaolinite respectively. The reason why Cu ion adsorption on these soils followed this trend is not understood. Further investigation is recommended to explain this behavior, presumably associated with the interaction between Cu ion and soils.

Distribution coefficient (Kd) and adsorption

Fig.3 shows that in 180 mins distribution coefficient (Kd) value which indicate attraction to soil were higher at Ikom (665.6 mL/g). While in 60 mins it was higher at Ishiagu (613 mL/g). Higher Kd value indicates stronger attraction to the soil solids and lower susceptibility to leaching loss. The greater distribution coefficient values in 180 mins at Ikom than other soils indicate that Cu ion has a greater affinity on this soil while it has a greater affinity on Ishiagu in 60 mins. This is attributed to higher organic carbon of these soils than Ihiagwa. This is in line with Erenturka and Malkocb (2007) who stated that variation in distribution coefficient is mainly related to the amount of organic matter (organic carbon) in the soils. The interpretations mentioned above are reasonable in principle. The Kd values show similar tendency with the adsorption percentage. This result is consistent with the adsorption of Ni (II) on oxidized multi-walled carbon nanotube (Shitong et al., 2008) and adsorption of Pb (II) by variable charge soils (Nkwopara 2012). The Kd showed no regular pattern with contact time.

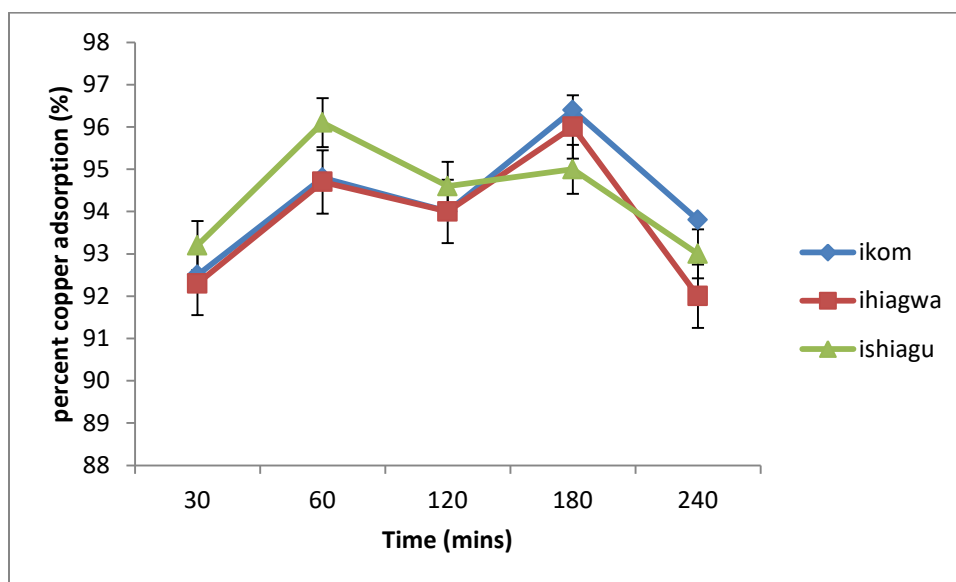


Fig. 2: percent adsorption of copper at different time interval

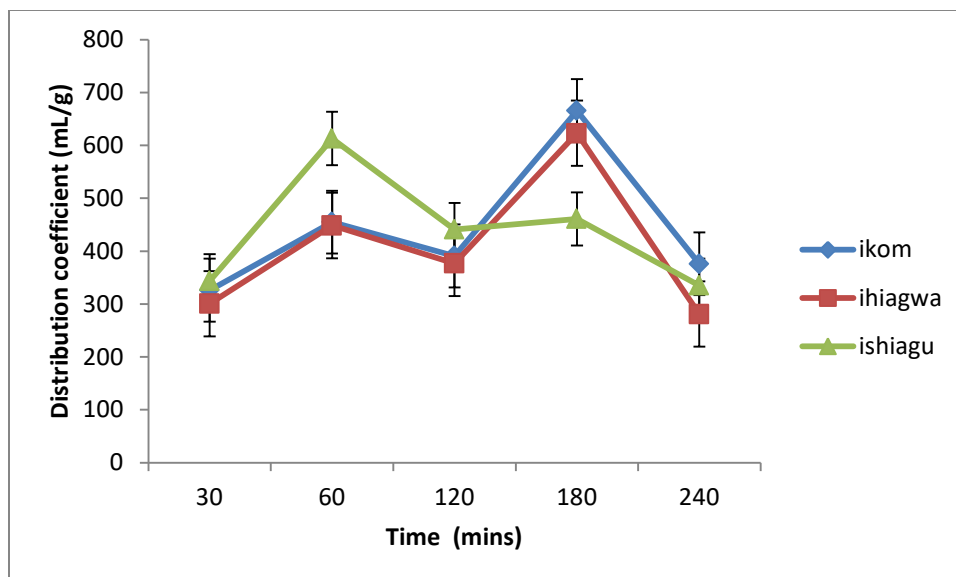


Fig 3: Distribution coefficient of copper at different time interval

Relationship between adsorption and soil properties

The relationship between adsorption and selected soil properties are presented in Table 2. Generally, physicochemical properties of the soil correlated positively with adsorption. A non-significant positive relationship ($p \leq 0.05$) was found between adsorption and soil properties ($r = 0.21, 0.14, 0.10, 0.15,$ and 0.16) for silt, organic matter, clay, pH and CEC respectively. This implies that as these soil properties increase adsorption of Cu by soil also increases. A non-significant negative relationship ($p \leq 0.05$) was found between adsorption and sand ($r = -0.17$). This implies that as sand particle increase

adsorption of Cu by soil decreases. This finding agrees with Nkwopara et al. (2018) on adsorption of Pb ion onto bentonite and soil of Owerri. Mbarki et al. (2008) reported that there was higher concentration of heavy metal in shoot and roots of plants grown on sandy soils than clay soils. Clay soils reduced the heavy metals availability to plants by adsorption of these metals. Also metals become adsorbed on surface of organic matter and this agrees with the positive correlation of organic matter with adsorption.

Table 2: Relationship between soil properties and adsorption

Soil properties	r	r ²	Significant level
CEC	0.16	0.58	NS
Clay	0.10	0.01	NS
Organic matter	0.14	0.02	NS
pH	0.15	0.02	NS
Sand	-0.17	0.03	NS
Silt	0.21	0.05	NS

NS= Not significant

Conclusion

Copper adsorption was minimum in all location at 30 mins and maximum at 180 mins with the exception of Ishiagu which was highest in 60 mins. Soils of Ishiagu will be less polluted with copper than Ikom and Ihiagwa within 120 mins while Ikom will be less polluted with copper than Ishiagu and Ihiagwa after 120 mins. Copper had greater affinity on Ikom at 180 mins but at 60 mins it had greater affinity on Ishiagu. The relationship between adsorption and selected soil properties showed that the intensity or

rate of adsorption of these soils was mostly influenced by soil pH, organic matter, clay, and CEC. From the study, it implies that adsorption probably increased with time but not in a progressive pattern upto 180 mins and then decreased.

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