

Copper Mobility in Three Nigerian Cocoa Soils as Affected by Different Organic Ligands

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Abstract: Desorption of Cu and low molecular weight dissolved organics are primary factors that impact fate and mobility of Cu in soils. To improve prediction of the toxicity and treat from Cu contamination in soil, it is expedient that time-dependent desorption behavior be understood. In this work, the effect of three organic ligands (citrate, malate and succinate) on the kinetics of Cu desorption in contaminated Ibadan, Owena and Ikom soils with different properties was studied using different kinetic models. Citric acid consistently desorbed larger amount of copper from the studied soils within the experimental conditions than malic and succinic acids. Based on coefficient of determination, the pseudo second order model best fit the description of desorption of Cu in Ikom, Owena and Ibadan soils. This information is critical since Cu-based fungicide is the main pesticide used by Nigerian cocoa farmers in controlling the attack of black pod disease in cocoa production which eventually may be a source of ground water contamination.

Key words: Cocoa copper • Desorption • Nigeria soils and organic ligand

INTRODUCTION

Agriculture in Nigeria economy has contributed immensely to rural development, industrial material, food security and non-oil foreign exchange earnings. Nigeria is currently the fourth largest producer of Cocoa (*Theobroma cacao*) with 190 metric tones in 2008. Cocoa is a crop of economic importance with more than 650,000 ha being cultivated in Nigeria [1]. It ranked first amongst agricultural export crops in its contribution to foreign earnings [2]. General and localized study have identified that the greatest factor responsible for the dwindling of cocoa production level in Nigeria is the ravages caused by black pod disease caused by *Phytophthora palmivora* and *P. mergakaya*. The major economic loss is from the infection of the pods which in turn affect the quality of the beans within the pods. Nigerian cocoa farmers make use of copper based fungicide which is believed to be the fastest and most reliable means of arresting the situation. The incidence of black pod disease is an annual occurrence and the degree of prevalence depends on the rate of precipitation and humidity. This naturally calls for annual application of copper based fungicide if the farmers must make harvest of cocoa pods at the end of the year. In other words, average Nigerian cocoa farmers apply Cu-based fungicide at least eight times in a year. The implication of this act is the accumulation of copper

which is a heavy metal in the soil. The accumulated copper concentrations in agricultural soils have reached 110 to 1500 mg kg⁻¹, compared with 20 to 30 mg kg⁻¹ background levels [3]. Because copper is considered as a hazardous metal and is included in the EPA's list of priority pollutants, the USEPA and the European Union have established maximum copper limits for soil and for bio-solid to be applied to fields. The current soil clean up criteria for copper in the USA is 600 mg kg⁻¹ [4] and the upper limit of total soil Cu set by the European union for receiving Cu-containing sewage sludge is 140 mg kg⁻¹ [5]. Fate and bioavailability of metals in soils is controlled by three main processes: (i) removal of metal from the soil solution by sorption into soil particles.(ii) release of the metal from the soil particles to the soil solution (desorption) and (iii) precipitation -dissolution of the metal as an independent phase in the soil matrix [6, 7]. Most scientists often rely on maximum adsorption level and neglect desorption behavior to predict the fate and transport of contaminants such as copper in the environment. This is unfortunate since once a soil is contaminated, desorption is an important process that controls the bioavailability of the contaminants. Thus, in order to improve remediation strategies, risk assessments and make better predictions about the mobility of contaminants, it is critical that time-dependent metal desorption behavior on soil be understood.

Low molecular-weight organic acids originated from decomposition of soil organic matter in the upper soil horizons play an important role in the fate of metals [8, 9]. The anions of low molecular weight organic acids can form soluble complexes with metal cations [10] and modify the fixation of metals by soil organic matter, oxides, clays and enhance their release [11]. Report on the effects of the organic ligands on desorption of metal exist [12]. However, information about the effect of organic ligands on desorption of copper in Nigeria cocoa soils do not exist at the moment. The phytotoxicity of copper depends on its bioavailability, which is closely related to the distribution of Cu in different chemical forms. Copper in soil may exist in various forms like: water soluble, exchangeable organically bound, associated with carbonates and hydrous oxides of Fe, Mn and Al and residual. It is therefore necessary to investigate the effect of three different organic ligands of low molecular weight on copper desorption behavior of selected Nigerian cocoa soils from different ecological of zones. Information obtained from this study will give insights to scientists that may lead to improved remediation strategies and risk assessments.

MATERIALS AND METHODS

Soil samples were collected with soil auger at 0-30 cm depth from uncultivated adjacent forests to cocoa farms in Ibadan, Owena and Ikom which represented the three cocoa ecological zones in Nigeria. The samples were crushed and sieved with 2 mm sieve. Sub-sample of the soils was treated with 100 mg kg⁻¹ Cu as CuSO₄. After adding copper, the soils were incubated at field capacity for 12 weeks, during which the soils were subjected to eight wet-dry cycles. After 12 weeks, the soils were air dried, crushed to pass through a 2 mm sieve and stored in polyethylene bag for chemical analysis. Kinetic batch experiments were carried out by adding 10 ml of organic acid (3 mM) to 1 g of contaminated soil samples in a reaction vessel unit. The mixtures were agitated on a mechanical shaker at selected time intervals (5, 10, 20, 40, 60, 120 and 240 minutes) and an aliquot of 5 ml was removed and filtered. The filtrate was analyzed for Cu using atomic absorption spectrophotometer and a number of five different kinetic models were applied to describe desorption. The kinetic experiments were carried out at 25°C temperature.

pH was measured electrometrically with glass electrode pH meter in water using soil: water ratio of 1:2.5. Organic carbon was determined by the Walkley-Black procedure [13]; total nitrogen by microkjeldahl digestion,

while available phosphorus was determined colorimetrically by the Molybdenum blue method [14]. The exchangeable cations were extracted by leaching 5 g soil with 50 ml of 1N ammonium acetate at pH 7 [15]. The potassium and sodium in the leachate were determined with a flame photometer (Corning EEL model 100) and the calcium and magnesium was determined with atomic absorption spectrophotometer (Hitachi model 207).

Kinetic Modeling: Five kinetic models were applied to the desorption data to better understand the effects of organic liquids and time on the desorption process. The five equations are as follows:

Elovich Equation:

$$q = (1/\alpha) \ln(a\alpha) + \left(\frac{1}{\alpha}\right) \ln t \quad (1)$$

Where:

q = the amount of adsorbate released in time t

a = a constant

α = a constant, related to the initial velocity of the reaction. Thus a plot of q versus ln t should give a linear relationship with the slope of (1/α) and intercept of ln (1/α) ln (aα)

Parabolic Diffusion Equation:

This equation may be written: $q = a + K_d t^{1/2}$

Where:

q = The amount of Cu desorbed in time t

a = a constant

K_d = apparent diffusion rate coefficient.

Thus, a plot of q versus t^{1/2} s should provide a linear relationship if the reaction conforms to parabolic diffusion law. 'a' is the slope and 'k_d' is the intercept.

Modified Freundlich Equation: The modified Freundlich equation according to Kuo and Lotse, [16] is in the form:

$$q_t = K_d t^{1/m}$$

And the Linear Form of this Equation Is:

$$\log q_t = \log K_d + 1/m \log t$$

Where:

q_t = desorbed Cu in time t (min⁻¹)

t = reaction time (min)

K_d = desorption rate coefficient (min⁻¹) and

1/m = constant.

Thus, a plot of $\log q_t$ versus $\log t$ should give a linear relationship if the reaction conforms to modified Freundlich model. $1/m$ is the slope while k_d is the intercept. These equations have been widely applied in desorption studies in soils and soil components, even though, the equations are empirical and yield only apparent rate parameters.

Pseudo Second-Order Rate: The reaction rate of a chemical reaction is defined as the change in concentration of a reactants or product per unit time. The concentrations of the products do not appear in the rate law because the reaction rate is being studied under conditions where the reverse reactions do not contribute to the overall rate. The reaction order and the rate constant must be determined by the experiment. Ho [17] resented a sorption pseudo-second order rate law expression showed how the rate depends on the Sorption capacity on solid phase but not the concentration of the sorbate.

$$\frac{dq_t}{dt} = k(q_e - q_t)^2$$

Integrated pseudo-second order rate law can be obtained from equation (1) for the boundary conditions $t = 0-t$ and $q_t = 0-q_t$ gives:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + Kt \quad (2)$$

Equation (2) can be rearranged to obtain a linear form:

$$\frac{t}{q_e} = \frac{1}{kq_e^2} + \frac{1}{q_e} \quad (3)$$

Where q_e is the amount of sorbate sorbed at equilibrium (mg kg^{-1}), t is the reaction time (min); q_t is the amount of Cu desorbed at time t (mg kg^{-1}); K is the equilibrium rate constant of pseudo- second order sorption. Ho's pseudo-second order rate law shows how the sorption capacity of sorbate depends on time. If the equilibrium sorption capacity of sorbate and the rate constant 'k' are known, then the sorption capacity of sorbate at any time can be calculated using the linear form equation, Equation (3) plotting $\frac{t}{q_e}$ versus t will give a straight line with slope $1/q_e$ and qt intercept $1/q_e^2$

Power Fraction Model:

The power fraction model has its linear equation as:

$$\ln q_t = \ln a + b \ln (t)$$

Where:

- q_t = desorbed Cu in time t
- a = desorption rate coefficient.
- b = constant
- t = reaction time.

A plot of $\ln q_t$ versus $\ln t$ should give a linear relationship if the reaction conforms to power fraction model. From the linear plot, 'b' is the slope while 'a' is the intercept.

Statistical Analysis: All data were processed by Microsoft excel (Microsoft 2007).

RESULTS

Physicochemical properties of the studied soils are presented in Table 2. Result showed that Owena and Ibadan texture soils are sandy loam while Ikom soil is clayed with high Fe content. Ikom soil was also found to be higher in organic carbon than the two other soils.

The effect of time on desorption of copper from the three studied soils by using different organic ligands is presented in Figure 1. A linear relationship of Cu release versus time was observed in the soil samples for all the organic acids (citric, succinic and malic). There was no desorption of Cu by succinic and malic acids in Ikom soil. Only citric acid was able to desorb Cu from Ikom soil. For citric acid, desorption of Cu was highest in Owena soil but least in Ikom soil.

For succinic acid, desorption was higher in Owena soil than Ibadan soil while no desorption in Ikom soil. In case of malic acid, desorption of Cu was higher in Ibadan soil than Owena soil. The result of desorption of Cu in the three studied soils showed that there is linear relationship between the amount of copper desorbed and time. This infers that desorption of copper from the studied soils by citric, malic and succinic acids is time dependent.

For the different soils, Cu desorption followed the release order: citric acid > succinic acid > malic acid. The sequence of amount of Cu released by citric acid is in accord with the stability constant of Cu-ligand complex (Table 2) but the release of Cu from Owena and Ibadan soils by malic acid was not in accord with the stability constant of Cu-ligand complex (Table 2). The inability of succinic acid and malic acid to desorb Cu from Ikom soil within the extraction conditions and time might be due to the high clay content of this soil which enhanced a strong bond between the metal and the charged clay edges.

Table 1: Some properties of organic ligands used in the study

Organic acids	Chemical formula	Molecular weight (g)	Ligand form
Malic	$\text{HO}_2\text{CCH}_2\text{CH}(\text{OH})\text{CO}_2\text{H}$	134.09	H_2L
Succinic	$\text{HOOCCH}_2\text{CH}_2\text{COOH}$	118.09	H_2L
Citric	$\text{C}(\text{OH})(\text{COOH})(\text{CH}_2\text{COOH})_2$	192.13	H_3L

Table 2: Physicochemical properties of the studied soils

	Ca	Mg	K	Na	P	N	C	pH	Fe	Clay	Silt	Sand
Soil	cmol kg ⁻¹				mg kg ⁻¹	%			mg kg ⁻¹	%		
Ibadan	3.30	0.48	0.43	1.26	13.2	0.17	1.66	6.81	7.2	15.2	14.6	70.2
Owena	5.38	0.96	1.82	1.10	20.1	0.21	1.64	6.73	7.2	13.2	17.3	69.5
Ikom	3.25	2.10	0.91	0.89	26.8	0.26	2.25	5.40	15.0	75.4	10.5	14.1

Table 3: Kinetic modeling parameters for Elovich, Parabolic diffusion and Freundlich

Organic ligands	Elovich			Parabolic diffusion			Freundlich		
	a	b	R ²	a	b	R ²	K _d	1/m	R ²
IKOM									
Citric	0.49	-0.26	0.91	0.13	0.58	0.70	-0.61	0.46	0.79
OWENA									
Malic	0.08	0.24	0.54	0.02	0.41	0.36	-0.57	0.17	0.50
Succinic	0.65	-0.05	0.81	0.16	1.11	0.59	-0.29	0.39	0.77
Citric	0.58	0.68	0.87	0.15	1.66	0.70	0.06	0.23	0.87
IBADAN									
Malic	0.10	0.32	0.88	0.02	0.51	0.74	-0.40	0.14	0.81
Succinic	0.31	-0.13	0.88	0.08	0.38	0.71	-0.70	0.40	0.85
Citric	0.32	0.51	0.94	0.01	1.01	0.84	-0.10	0.20	0.94

Table 4: Kinetic modeling parameters for Pseudo second-order and power fraction

Organic ligand	Pseudo second-order			Power fraction		
	1/qe	1/Kqe ²	R ²	a	b	R ²
IKOM						
Citric	0.43	7.38	0.99	0.46	-1.41	0.77
OWENA						
Malic	1.60	8.34	0.99	0.18	-1.35	0.52
Succinic	0.31	3.87	0.99	0.39	-0.68	0.76
Citric	0.27	2.18	0.99	0.23	0.15	0.87
IBADAN						
Malic	1.08	1.47	0.85	17.10	-79.12	0.45
Succinic	0.17	20.35	0.46	0.40	-1.61	0.85
Citric	0.44	4.50	0.99	0.20	-0.25	0.94

The introduction of organic ligands to desorption system may cause the change of the surface characteristics of soils competitive distribution of metal ions between soil surface and organic ligands in the solution and partly dissolution of minerals in soils. On the overall, the release of Cu was mostly enhanced in the presence of citrate ligand under the reaction conditions studied. To further assure the effectiveness of organic ligands on Cu release, the results were modeled using several kinetic equations.

Kinetics: The use of kinetic models was for qualitative compares of data sets. Often, multiple models can fit the same set of kinetic data [18] therefore; it is intended only to investigate the efficacy of these models in pointing out differences in Cu release trends. Tables 3 and 4 give the values of the experimental data.

Elovich Equation: The empirical Elovich equation [19] was used to describe the Cu desorption rate. Elovich equation plots of Cu desorbed vs ln of reaction time 't' at 25°C for Ikom, Owena and Ibadan soils as affected by citric,

malic and succinic acids are shown in Figure (3). A linear relationship exists between q and $\ln t$ for each of the three organic ligands used. Elovich equation parameters were determined from the slope and intercept of the linear plots. Parameters for the three soils and organic acids are shown in Tables 1 and 2 respectively. The 'b' values listed in Table 3 for Ikom, Owena and Ibadan soils were highest in the presence of citric acid. In Elovich equation, a decrease in 'b' indicate a reduction in desorption reaction rate [19]. Therefore, the rate of Cu desorption from Owena and Ibadan soils increased as a result of using citric acid followed by malic and succinic acids. Malic and succinic acids did not desorb Cu within the experimental condition used. Citric acid had a negative value for 'b' (-0.26) in Ikom soil. Elovich equation fit Ikom and Ibadan soils plus citric acid ($R^2 > 0.91$). The information provided by 'b' suggested that the presence of citric acid will increase Cu desorption; however, these parameters are dependent on soil type and reaction conditions.

Parabolic Diffusion Equation: The parabolic diffusion model was also used to describe the kinetic data of Cu released from the soils as affected by three organic acids at 25°C are shown in Figure 5. A linear relationship exist between Cu released and $t^{1/2}$ for citric acid in the three studied soils but a non linear relationship between Cu released at $t^{1/2}$ for succinic and malic acids in Owena and Ibadan soils. Parabolic diffusion law parameters were determined from the slope and the intercept of the linear plots. Parameters of the three soils as affected by citric, succinic and malic acids are shown in Table 3. The apparent-Cu diffusion rate coefficient 'b' in the parabolic diffusion law is considered a measure of the relative rate of Cu release. The 'b' values for citric acid followed the order of Owena > Ibadan > Ikom with the values of 1.66, 1.01 and 0.58 respectively (Table 1). In addition the 'b' values for succinic acid was higher in Owena soil than Ibadan soil with the values of 1.11 and 0.38 respectively while the 'b' values for malic acid was higher in Ibadan soil than Owena soil. The lowest values of 'b' for citric acid in Ikom soil (0.58) compared with Owena (1.66) and Ibadan (1.01) soils could be as a result of its higher organic matter content, clay content and CEC. The low R^2 values for desorption of Cu from the studied soils by citric, malic and succinic acids ranged between 0.36 and 0.84. These values are low and therefore, made parabolic diffusion equation unsuccessful in describing the kinetics of Cu released by the three studied soils as affected by the three organic acids used. Linear relationships, an indicator that desorption processes are diffusion

controlled [20] are evident in the three soils as affected by citric acid. Diffusion controlled desorption was also evident in Ibadan soil as affected by succinic acid. Malic acid did not give linear relationship in any of the studied soils. The diffusion coefficient 'b' was greatest in the soil with a light texture and lowest organic matter content, as soils with more heterogeneity are more likely to have an increase in transport-limited processes. Calculated diffusion coefficients were higher for soils plus citric acid compared with the two others indicating that diffusion rates were faster. The diffusion coefficients were much lower in malic and succinic acids influenced desorption for the soils studied. Such an observation suggest that the influence of diffusion in desorption of copper by succinic and malic acids in the studied soils is low compared with citric acid. However, the type of diffusion that took place cannot be determined in any of the cases. The linear portion of the plot for the range of contact time between the organic acid and the soil does not pass through the origin. This deviation from the origin or near saturation may be due to the variation of mass transfer in the initial and final stages of desorption [21] such a deviation from the origin indicates pore diffusion is the only controlling step and not the film diffusion.

Modified Freundlich Model: The modified Freundlich model [16] was also used to described the Cu desorption data. Modified Freundlich plot of log Cu desorbed versus log of reaction time for the Ikom, Owena and Ibadan soils at 25°C as affected by the three organic ligands are shown in Figure 5. Linear relationships exist between Cu desorbed and log t for the three studied soils. The modified Freundlich equation parameters K_d and $1/m$ were calculated from the intercept and the slope of the linear plots. The values of desorption rate coefficient ' K_d ' and $1/m$ for the soils are shown in Table 3. In general, the desorption rate coefficient ' K_d ' values listed in Table 3 as a result of citric acid addition were the highest in comparison with the succinic acid and malic acids in the same soil. From linear regression, the results from the study showed low coefficient of determination for modified Freundlich model.

Pseudo Second-order Equation: The pseudo second-order was also used to describe the kinetics data of Cu release from the soils as affected by three organic ligands at 25°C are shown in Figure 3. Linear relationship exists between t/qt of Cu desorbed and time of reaction. Pseudo second-order-parameters were determined from the slope and intercept of the linear plot. Parameters of

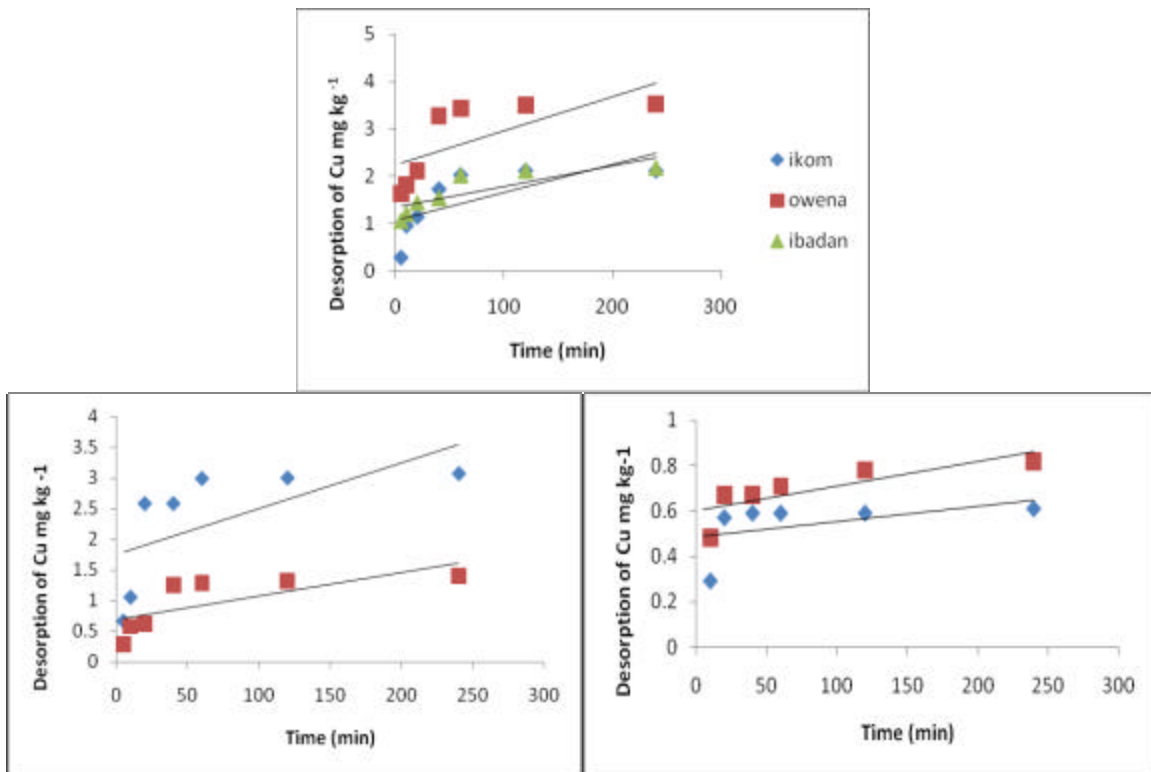


Fig. 1: Desorption of copper from soils by organic ligands.

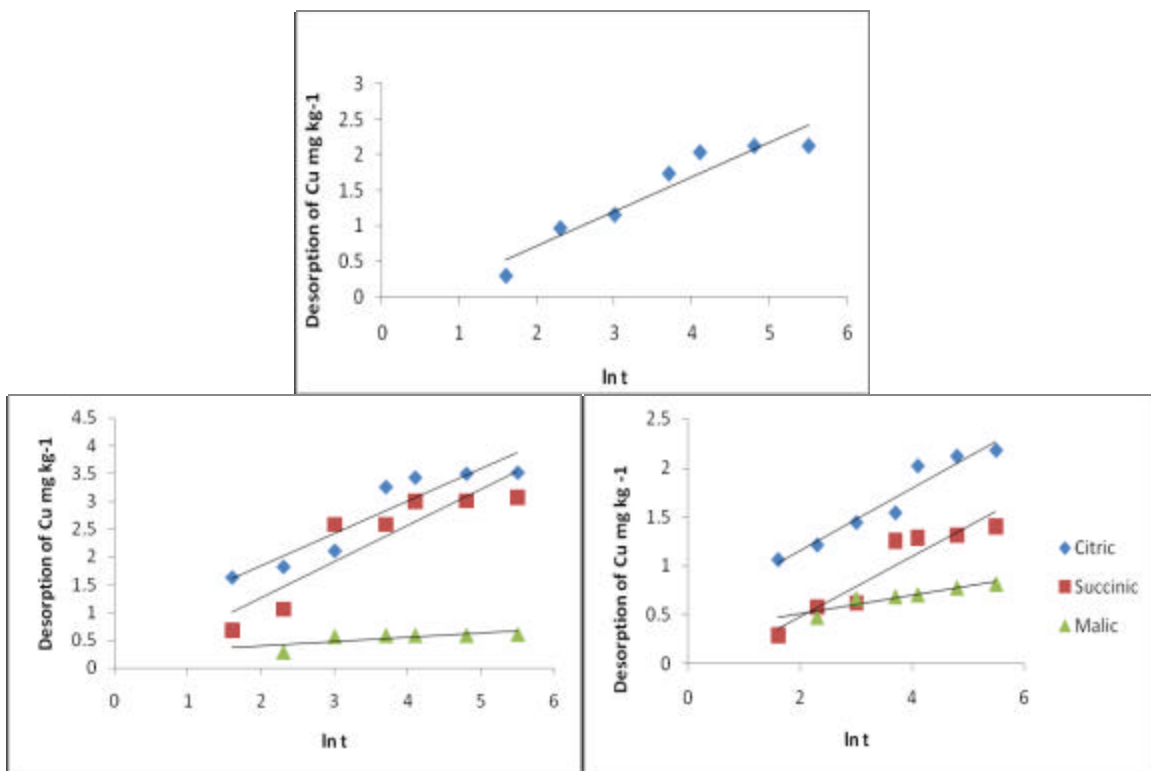


Fig. 2: Elovich equation.

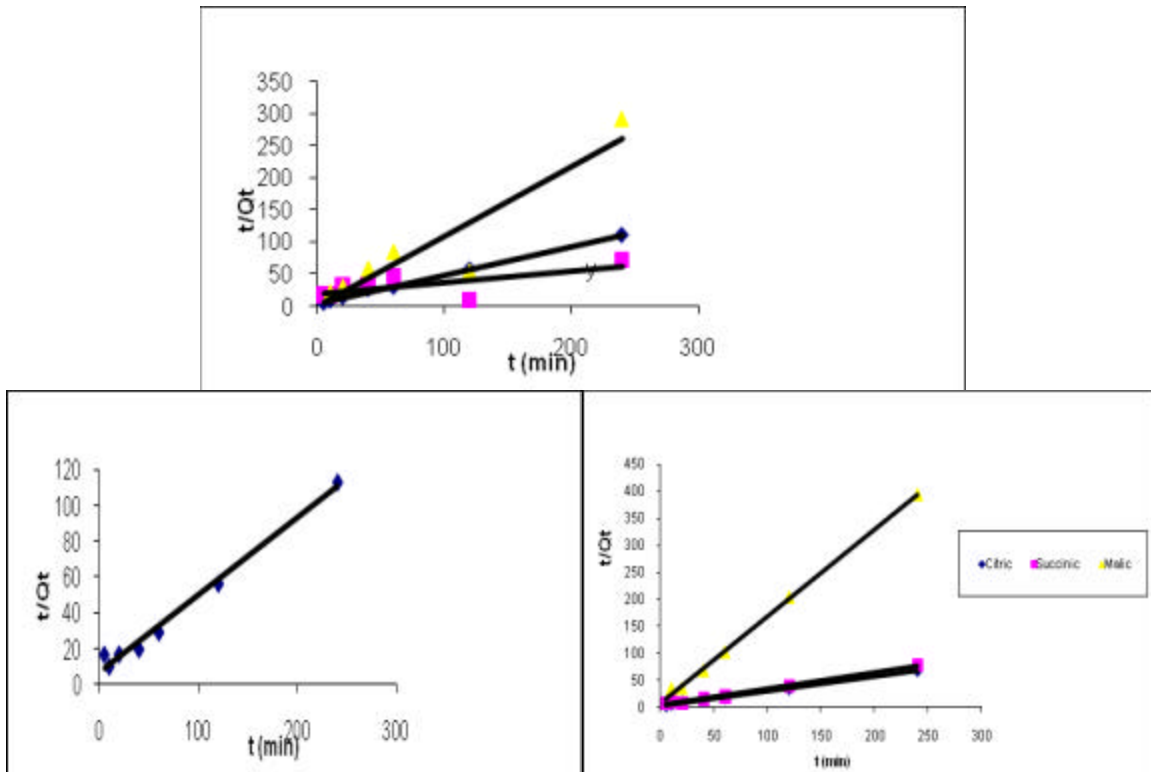


Fig. 3: Pseudo second-order kinetics.

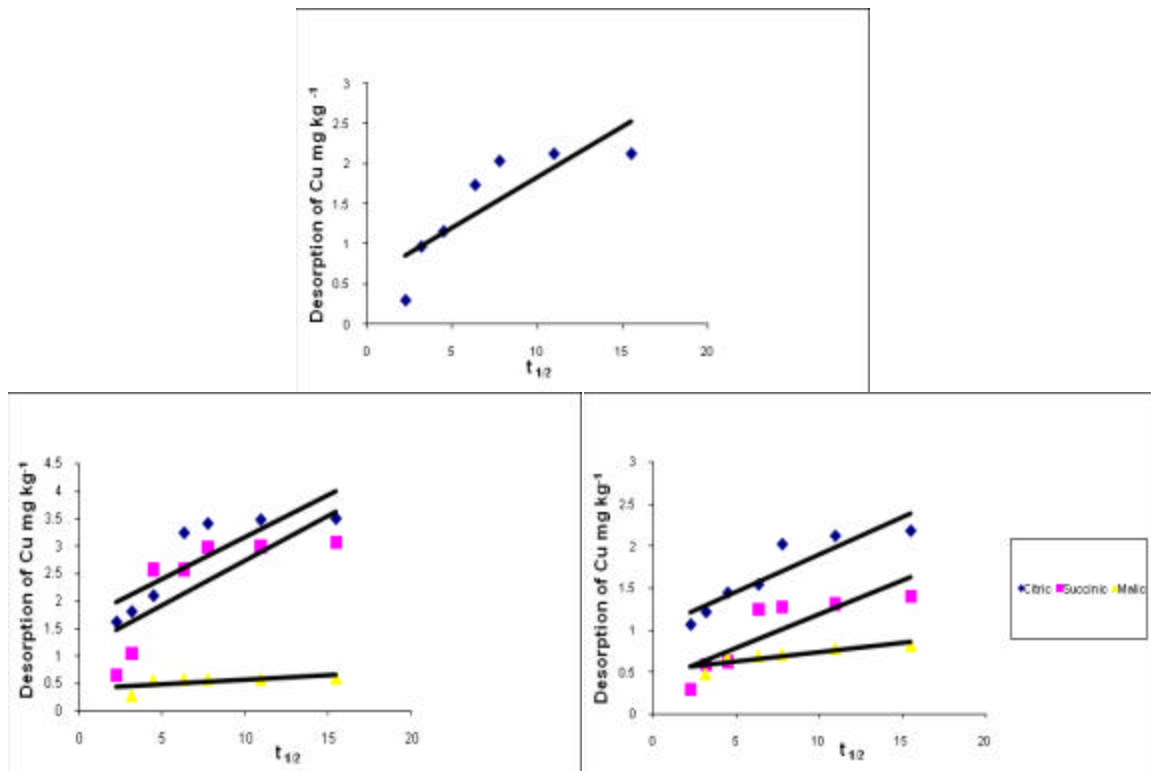


Fig. 4: Parabolic diffusion

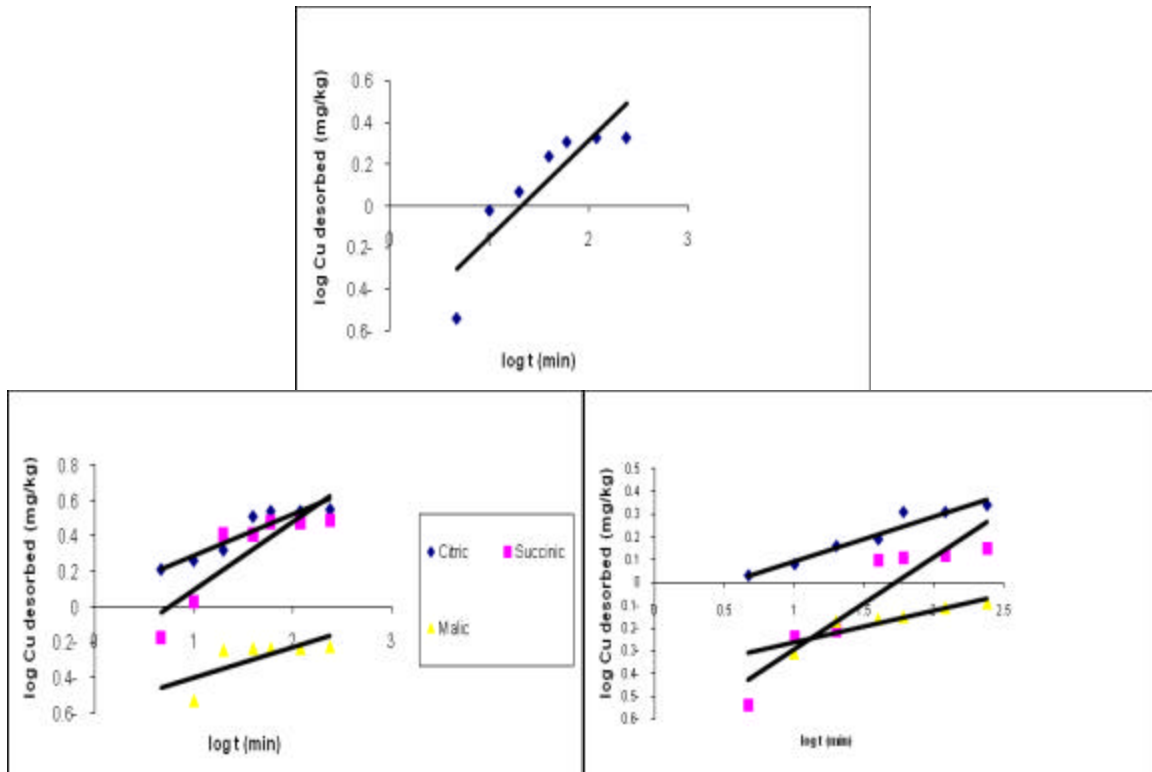


Fig. 5: Modified Freundlich equation.

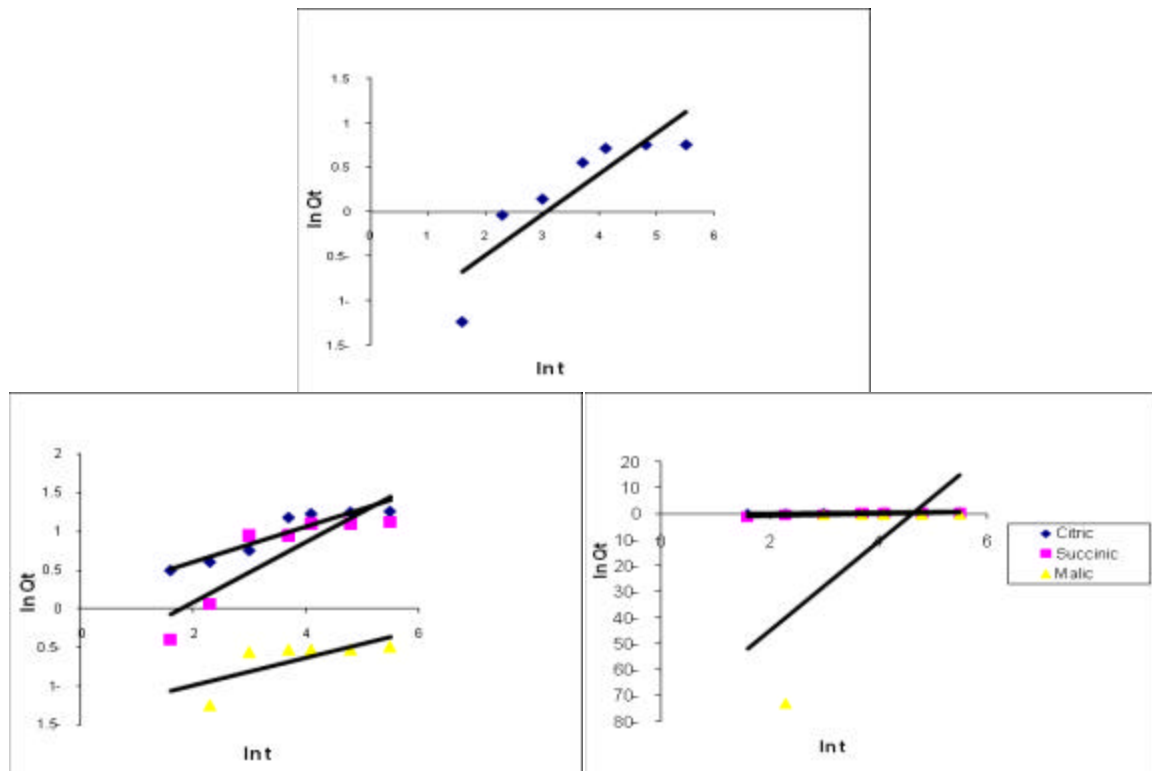


Fig. 6: Power fraction model

the three soils as affected by citric, succinic and malic acids are shown in Table 4. The rate coefficient of the pseudo second-order-reaction was determined from the intercept $1/Kq_e^2$ of the plot while the $1/q_e$ was determined from the slope. Citric acid had the value $1/Kq_e^2$ in the order of; Ikom > Ibadan > Owena. Malic acid was in the order of; Owena > Ibadan while succinic acid was in the order of; Ibadan > Owena. The regression correlation coefficient values R^2 of the three organic ligands in the studied soils were high in Owena soil (Table 4) with an average value of 0.99. Citric acid gave R^2 value of 0.99 in all the studied soils. On the other hand, succinic and malic acids gave high coefficient of determination for citric acid in all the studied soils while succinic and malic acids showed high coefficient of determination in Owena soil. The high R^2 value confirm that the desorption data are well represented by pseudo-second order kinetics and supports the assumption behind the model that the adsorption of Cu into the soil matrix was due to chemisorptions.

Power Fraction Model: The power fraction model was also used to describe the Cu desorption data. Power fraction plots of \ln of desorbed copper versus \ln of reaction time 't' for the Ikom, Owena and Ibadan soils at 25°C as affected by the three organic acids are shown in Figure 6. Linear relationship only exist in Owena soil between \ln desorbed copper and ' $\ln t$ ' for the three organic acids. Desorption rate coefficient 'b' values listed in Table 4 were negative values except for citric acid in Owena soil. The low values of the linear regression for all the ligands in all the soils indicated that power fraction model is not fit for the description of the desorption of Cu from Ikom, Owena and Ibadan soils as affected by citric, malic and succinic acids.

DISCUSSION AND CONCLUSION

Investigation has been made to study the effect of time on desorption of Cu from three different soils by using different organic acids as extractants. The quantity of copper released from soils followed the trend; Owena > Ibadan > Ikom. The low Cu desorption associated with the clay soil suggests that most Cu ions are specifically chemically sorbed by both organic matter and clay minerals. Organic matter at low levels has strong affinity for Cu [22]. McBride [23] proposed possible binding configurations of Cu^{2+} on complexes of oxide minerals and organic matter: (i) Cu^{2+} is bonded to the mineral surfaces only (inner-sphere complex); (ii) Cu^{2+} is bonded to the

organic matter that is adsorbed by the oxides at high levels (Type B tertiary complex); and (iii) Cu^{2+} act as a bridge cation between the oxides and the organic matter that is adsorbed at low levels (Type A ternary complex).

For all the studied soils citric acid had the strongest ability to desorb the desorbed copper. The difference in the effect of Cu desorption by organic acids is related to their chemical structures. Among the organic ligands used, ions of malic and citric acids carrying two or three $-COO^-$ group can form chelates with 5- or 6-member ring structure. The greater stability of the citrate complex led to the greater efficacy of citric acid in desorbing Cu from soils than succinic and malic acids, besides succinic and malic acids with smaller acid dissociation constant (pK_a values 4.16 and 3.46) provided fewer anions for complexing with Cu than citric acid (pK_a value 3.13) and thus may show smaller effect on metal desorption.

Results presented showed that organic ligands are effective chelators of sorbed metals and organic ligands may play an important role in the mobilization and phyto-availability of Cu in soils. Based on coefficient of determination, the pseudo second order model best fit the description of desorption of adsorbed Cu in Ikom, Owena and Ibadan soils as affected by citric, succinic and malic acids. Information obtained from this study will give insights to scientists and engineers that may lead to improved remediation strategies, disposal practices and risk assessment.

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