Sorption and Infiltration Potential of a Cationic Herbicide (Paraquat) in Three Cocoa Growing Soils in Nigeria

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Authors' contributions

This work was carried out in collaboration among all authors. Author PEA designed the study and wrote the manuscript. Author IAO provided information on paraquat and literature review while author SMO handled the chemical analysis of samples. All authors read and approved the final manuscript.

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ABSTRACT

Despite the ban of paraquat, its use among Nigerian farmers for weed control is still popular. Larger proportion of applied herbicide ends up in the soil matrix. Off-site transfer of the residual paraquat as contaminant to other environmental compartment depends on sorption process. In order to study the influence of soil characteristics on retention and infiltration of paraquat in cocoa soils, adsorption of paraquat in selected cocoa soils was carried out. In the course of the experiment, Owena, Ibadan and Ikom soils were equilibrated with paraquat solutions of different concentrations ranging from 100 to 800 mg paraquat kg^{-1} soil. Result showed that, Freundlich model gave better description of paraquat adsorption in the investigated soils than Langmuir model. The pseudo second order kinetic equation gave better description of the adsorption mechanism than pseudo first order. Statistical analysis showed that, aluminium oxide and clay mineral contents were the main soil physicochemical parameters that influenced paraquat sorption in the soils. The low values of groundwater ubiquity score obtained from the adsorption data showed that, the investigated soils were non leacher of paraquat. Hence, its guided and appropriate use may not cause underground water contamination.

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1. INTRODUCTION

The intensive use of pesticides on large areas of agricultural soil has given rise to concern about their fate in the environment. For many years, their presence as well as their environmental impact has attracted much attention due to the wide use of such compounds in agriculture and household applications [1]. Less than 1% of total applied pesticides reach the target pests, the vast majority being dispersed in the different environmental compartments (water, air and soil) but mainly in aquatic environment via agricultural runoff or leaching [2]. Application of herbicides on agricultural soils is a well-established and effective practice to control weed growth. They represent about 50% of the demand for agricultural chemicals; their prolonged use involves the risk of their retention in crops and soils. Soil is an ultimate reservoir for these products, whether applied directly or received indirectly from spray drift and residues of treated sites [3].

Paraquat (1, 1-Dimethyl-4, 4-bipyridine dichloride) is a non selective herbicide commonly used to control weeds in agricultural crop production in Nigeria. It is a quaternary nitrogen herbicide with a quick acting compound that destroys green plant tissue on contact and by translocation within the plant. It destroys plant tissue by disrupting photosynthesis and rupturing cell membranes, which allows water to escape leading to rapid desiccation of foliage [4]. It can also be translocated within the plant, increasing the likelihood of residues being accumulated in plant tissue. The use of paraquat on cocoa has been banned in some countries and restricted in others because of its toxicological effect on animals and human. When paraquat gets into the soil, it is readily and strongly adsorbed onto clay minerals and organic particles [5]. According to Koskinen and Harper [6], the capacity of a soil to adsorb or retain a pesticide is a key parameter controlling the extent to which the chemical will leach through the soils to groundwater. The process therefore, determines both the efficacy of paraquat in controlling target weeds as well as its environmental impact on the soil system. Paraquat as an herbicide is popular among Nigerian farmers including those that cultivate cocoa. Currently, Nigeria is the fourth largest producer of cocoa in the world with a production capacity of 250 metric tonnes (CBN, 2010). Though the European Union has banned the use of paraquat in cocoa plantations, personal interaction with some cocoa farmers in selected parts of the country showed that, some farmers still make use of paraquat for the control of weeds. After the application of herbicide, a larger proportion of the applied agrochemical goes to the soil and the portion that is absorbed by the weed during application returns to the soil after the decay of plant residue. The fate, bioavailability and potential environmental impacts of such herbicide is strongly determined by adsorption-desorption process within the soil system.

Adsorption is related to soil properties such as clay content, clay mineralogy and organic content [7]. When paraquat molecules bind to adsorption sites on clay and penetrate the inter-lattice regions of the expanding clay particles, the herbicide persist within the clay mineral thereby reducing its mobility and environmental impacts. In a situation where soil has low adsorption capacity for paraquat, its bioavailability and downward mobility in such soil will be high. The possibility of contaminating underground water (well and bore-hole water) especially where the water table is high will equally increase. Consumption of paraquat-contaminated water could pose health threat in human. However, information on sorption characteristics of paraquat in Nigerian agricultural soils is scanty. Hence, the study was aimed at determining the adsorption mechanism of paraquat in selected Nigerian cocoa soils with a view to determining sorption coefficients as a function of soil physicochemical properties.

2. EXPERIMENTAL DESIGN AND STATISTICS

Soil samples were collected with hand trowel at the depth of 0-5 cm from selected cocoa plantations in Owena (7°10'N 4°59'E), Ibadan (7°09'N, 3°50' E) and Ikom (5°52'N 8°48'E) substations of Cocoa Research Institute of Nigeria, Ibadan, Nigeria. The locations where sample collections were made have annual rainfall of 2,000 to 3500 mm. The samples were collected in five different points within each location and bulking of the samples was done to reduce sample size and to have adequate representation of individual location. The soil samples were air-dried and sieved with 2mm sieve. Sample analysis was done in triplicates.

2.1 Determination of Soil Physico-chemical Properties

The pH values of the samples were determined in distilled water using a soil-solution ratio of 1:1 [8]. Organic carbon was determined by the Walkley-Black wet oxidation method [9]. Exchangeable basic cations were extracted with neutral normal ammonium acetate with K and Na determined by flame photometry while Ca, Mg, Fe, Zn, Al and Mn were determined with Buck Scientific Atomic Absorption Spectrophotometer [10]. Particle size distribution was determined by the hydrometer method after dispersion with sodium hexametaphosphate [11]. Available Phosphorus was determined using Bray and Kurtz [12] method.

2.2 Standard and Reagents

All reagents used were of analytical grade while all the standard solutions were prepared with distilled water.

2.3 Adsorption Experiment

Adsorption experiment was conducted by equilibrating one gram (1 g) of the various soil samples with 15 ml solution containing 100, 200, 300, 400, 500, 600, 700 and 800 mg of paraquat in 0.01M $CaCl_2$ solution. The suspensions (in triplicate) were equilibrated in a mechanical shaker at pH 7±0.2 for 2 hours at the temperature of 25°C±2. After equilibration, the sample bottles and their contents were centrifuged at 4000 rpm for 20 minutes. The supernatants were filtered through Whatman filter paper No 1.2 ml of the supernatant was added to 10 ml of 1% NaS_2O_4 prepared in 0.1M NaOH and paraquat in the solution was determined by measuring the absorption at 600 nm with visible spectrophotometer WPA Biochrom. Paraquat concentrations were determined from the calibration graph obtained from the prepared paraquat standards. Correlation (R^2 = 0.99) was obtained from the graph. The quantity of the herbicide adsorbed by each soil sample was calculated from the difference between the concentration of paraquat in solution before and after equilibration. For the purpose of control, blanks were set up using the same solid-to-liquid ratios. Instead of adding paraquat solution to the soil, distilled water was added. The data generated from the sorption study were fitted into Langmuir and Freundlich equations.

2.4 Kinetics of Paraquat Adsorption

Study on the kinetics of paraquat adsorption was carried out by adding 25 ml of 60 mg paraquat L^{-1} solution into polypropylene sample bottles containing one gram (1 g) of each sample. The samples were then equilibrated on a mechanical shaker for 40, 60, 80, 120 and 140 minutes. At the expiration of each contact time, the sample bottles and their contents were transferred to the centrifuge. The samples were centrifuged at 4,000 rpm for 20 minutes. Each of the aliquot was filtered with Whatman filter paper No 1 and the concentration of paraquat in the equilibrium solution was determined using the same procedure described above. Data obtained from the experiment were fitted into Pseudo-First order, Pseudo-second order, mass transfer and intra-particle diffusion equations.

2.5 Quantification of Adsorbed Paraquat in Soil

The capacity of the various soils to retain magnesium was determined using the equation

$$Q = \frac{V\Delta C}{W} \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots(1)$$

where Q is the quantity of paraquat adsorbed in mg kg^{-1}, V is the volume of solution added to the sample in liter, ΔC is the difference between concentration of paraquat in solution before and after equilibration ($C_o - C_e$). Where C_o is initial concentration and C_e is concentration after equilibration. W is the weight of soil sample used in kilogram.

3. RESULTS AND DISCUSSION

3.1 Soil Physico-chemical Properties

Selected physico-chemical properties of the investigated soils are presented in Table 1. Calcium content of the soils ranged from 5.42-9.27 cmol kg^{-1}. All the values obtained for calcium in the three soils were adequate for cocoa cultivation being higher than 0.5cmol kg^{-1} which is the essential concentration of extractable calcium a soil must possess to support cocoa cultivation. Ikom soil had the highest value while Owena soil had the least calcium content. The extractable magnesium in the soils were moderately high enough to support cocoa production as the values obtained in the soils (1.35 -3.16 cmol kg^{-1}) were all higher than 0.8 cmol kg^{-1} which is the critical level of magnesium in cocoa soil [13]. Many researchers

have however, reported the deficiency of magnesium in some cocoa plantations in Nigeria. [14] reported magnesium deficiency in selected cocoa soils in Nigeria. [15] reported magnesium deficiency in tropical soils which was attributed to severe weathering, soil erosion and clay eluviations. [16] reported magnesium deficiency in selected cocoa plantations in Ibadan, Nigeria while [17] reported also reported magnesium deficiency in some cocoa plantations in Ondo State, Nigeria. The soil pH ranged from 5.10 to 6.85. The soil pH values obtained from the various soils show that Ikom soil is more acidic than Owena and Ibadan soils. The pH range is adequate for cocoa production since cocoa does well within a pH range of 5.0-7.5 [18]. Nitrogen content of the soil ranged between 0.08 and 2.16. Among the three soils, Ibadan soil alone had nitrogen content lower than the critical level (0.09%) for cocoa cultivation.

Potassium content of the soils ranged from 0.26 to 0.49 cmol kg^{-1}. Ibadan soil had the least K value (0.26 cmol kg^{-1}) which is lower than the critical level (0.03 cmol kg^{-1}) for cocoa cultivation [13]. The soil available phosphorus in the soils was between 7.90 and 11.40 mg kg^{-1}. Out of the three soils, only Ikom soil had available P above the critical (10 mg kg^{-1}) level. This is an indication of phosphorus deficiency in cocoa soils. Phosphorus is an important plant nutrient that

has been reportedly deficient in cocoa plantations in Nigeria. Low phosphorus content in south western Nigeria cocoa soil was reported by [19]. Particle size analysis showed that, Ikom soil had 75.40, 10.50 and 14.10% clay, silt and sand respectively Owena soil had 13.20% clay; 17.30% silt and 69.50% sand while Ibadan soil had 13.00, 14.00 and 73.00% clay, silt and sand respectively.

3.2 Effect of pH on Paraquat Adsorption

The effect of pH on adsorption of paraquat onto the studied soils was determined by adjusting the pH of the various soils to 2, 4, 7 and 9 using HCl to reduce and NaOH to raise soil pH. Result (Fig. 1) clearly demonstrated the effect of pH on the adsorption of paraquat. Paraquat adsorption onto the three soils increased with pH. In Owena soil, percentage of paraquat adsorption increased from 58.75% in soil sample with pH 2 to 67.21% in soil sample with pH 9. Similarly, adsorption increased from 52.94% in Ibadan soil having pH value of 2 to 70.59% in soil with pH 9. Also, percent pararquat adsorbed increased from 66.18% in Ikom soil with pH 2 to 85.30% in soil with pH 9. The percentage of paraquat adsorbed in Ikom soil at all pH levels considered in the study was higher than that of Owena and Ibadan which are loamy in nature.

Table 1. Soil physico-chemical properties

| Soil parameters	Ikom	Owena	Ibadan
Ca (cmol kg^{-1})	9.27±0.56	5.42±0.84	7.63±0.73
Mg (cmol kg^{-1})	3.16±0.11	1.78±0.04	1.35±0.10
Na (cmol kg^{-1})	0.52±0.01	0.21±0.02	0.26±0.03
K(cmol kg^{-1})	0.47±0.03	0.49±0.05	0.26±0.04
Al (mg kg^{-1})	0.58±0.07	0.36±0.01	0.30±0.02
Fe (mg kg^{-1})	15.00±1.00	7.00±1.10	7.50±0.86
Mn (mg kg^{-1})	8.52±0.87	2.64±0.66	3.86±0.57
Cu (mg kg^{-1})	0.78±0.06	0.72±0.03	0.84±0.08
P (ppm)	11.40±0.20	9.81±0.31	7.90±0.42
pH (water)	5.10±0.75	6.85±0.52	6.70±0.72
N (%)	2.16±0.45	0.92±0.02	0.08±0.01
Organic C (%)	2.25±0.84	0.96±0.07	0.84±0.05
CEC(cmol dm^{-3})	5.36±1.20	7.10±1.04	4.68±0.96
Sand (%)	14.10±2.50	69.50±2.68	73.00±3.42
Silt (%)	10.50±1.24	17.30±3.20	14.00±1.04
Clay (%)	75.40±3.00	13.20±1.20	13.00±1.07

Key: ± = SD; n=3
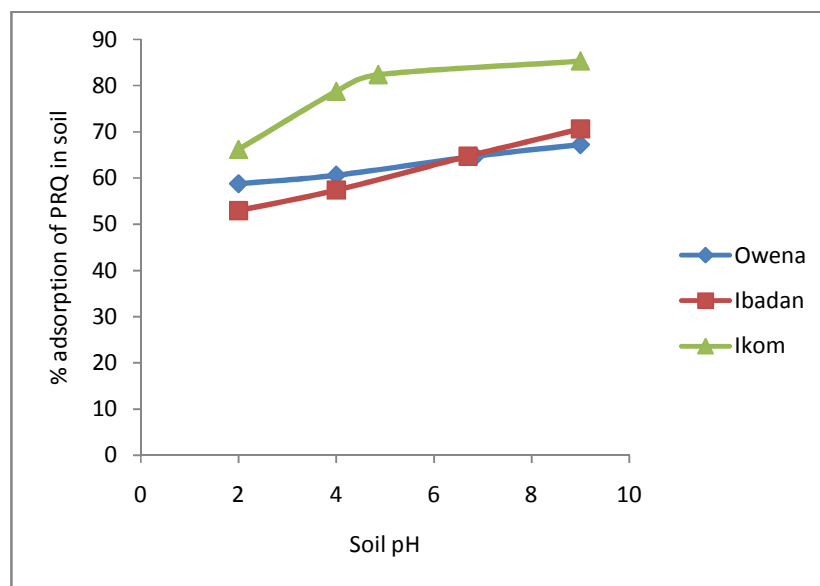
Fig. 1. Effect of pH on paraquat adsorption

It is well known that, as pH increases, the adsorption of cationic species in solution also increase in response to the increased number of negatively charged sites that become available as a result of the loss of H^+ from the soil surfaces [20]. The surface of activated clay exhibit negative charges under the experimental conditions of pH greater than 2 which is mainly due to the variable charges from the pH dependent surface hydroxyl sites [21]. Observation showed that, adsorption of paraquat onto the studied soils became steady at pH values above 7 (Fig. 1). Similar observation was recorded by [22] where adsorption of paraquat onto diatomaceous earth increased with pH. Similarly, [23] reported significant increase in paraquat adsorption onto swine-manure-derived biochar as the solution pH increased. The report of Tsai and Chen [23] was slightly different in the sense that, paraquat adsorption tended to decrease with increase of pH values from 7.5 to 9.0. They attributed such occurrence to the electrostatic repulsion between the positively charged surface and the positively charged adsorbate molecule.

The environmental implication of this simply means that, any agricultural practice or anthropogenic activity that lowers soil pH may increase the mobility and bioavailability of paraquat which will ultimately increase the risk of underground water contamination and bioavailability.

3.3 Effect of Initial Paraquat Concentration

The effect of initial paraquat concentration on adsorption was evaluated in the studied soils. Result (Fig. 2) showed a steady increase in the adsorption of paraquat as solution concentration of paraquat increased. However, at certain stage, the percentage of adsorbed paraquat dropped. For instance in Ibadan soil, the percent adsorbed paraquat increased from 40 to 63.13% when solution concentration was 300 and 700 mg paraquat L^{-1} respectively. But thereafter, the percent adsorption dropped to 61.43 when solution concentration increased to 800 mg paraquat L^{-1}. In Owena soil, paraquat adsorption increased from 41% at an initial concentration of 300 mg paraquat L^{-1} to 63.91% at solution concentration of 600 mg paraquat L^{-1}.

When the initial concentration of paraquat in solution increased to 700 mg L^{-1}, the adsorption dropped from 63.91 to 55.81%. The adsorption efficiency further dropped to 50% when the initial solution concentration increased to 800 mg L^{-1}. It therefore, implies that, Owena soil attained maximum adsorption efficiency at solution concentration of 600mg Paraquat kg^{-1} soil while Ibadan soil attained maximum adsorption efficiency at solution concentration of 700 mg paraquat kg^{-1} soil. Ikom soil had 87% adsorption efficiency when the initial concentration was 400 mg L^{-1}. The percent adsorbed herbicide dropped

to 80 when the initial concentration increased to 500 mg L^{-1}. The adsorption efficiency however, increased to 88% when the initial paraquat concentration in solution increased to 800 mg L^{-1}. The observed general decrease in adsorption efficiency as the initial concentration increased was an indication of saturation of the adsorption sites with cationic paraquat as the initial concentration increased. According to Tsai and Chen [22], adsorption rate decreases gradually approaching a plateau due to continuous decrease in the concentration driving force. At higher solution concentration of adsorbate, lower adsorption yield is due to the saturation of adsorption sites which is a consequence of increase in the number of ions competing for available binding sites [24].

The comparative higher adsorption efficiency observed with Ikom soil was a reflection of clay content of the soil. Among the studied soil types, Ikom soil had the highest clay content (75.40%) while Owena and Ibadan soils had 13.20 and 13% respectively (Table 1). It is known that adsorption through the interaction of paraquat with clay and expanding lattice, occurs with the exclusion of the water normally associated with mineral surface [25]. X-ray diffraction studies by [26,27] have shown that, when paraquat is adsorbed, it adopts a planar configuration parallel to the surface of the clay lattice. At the same time, the expansion of the lattice needed to accommodate the adsorbed paraquat is less than the normal Vander Waals' thickness of an ion.

Pesticides are often adsorbed to clay or organic matter constituents of soils at sites that are largely negatively charged [28]. Ikom soil had a comparative advantage over the two other soils based on the factors that mainly determine adsorption intensity. Data obtained from physicochemical analysis of the soil samples shows that Ikom soil had higher organic carbon (2.25%) than Owena and Ibadan soils with 1.96 and 1.84% organic carbon respectively. Muhammad et al. [21] reported that, the adsorption of paraquat was more in clay loam soil which was 2.8 times higher in organic matter than the rest soils. Knight and Tomlinson [26] reported that, paraquat adsorption was a property mainly of clay minerals, while organic matter would exert only a very small influence on its adsorption. The negative charges on the hydroxyl group bonded to Fe and Mn in soil also influenced paraquat sorption capacity of Ikom soil compared with Owena and Ibadan soils. This was reflected by the linear correlation of soil physicochemical properties and K_f. Result shows positive correlation between Fe, Mn and adsorption capacity (K_f) (Table 3). Table 1 shows that, Ikom soil had the highest concentration of Fe and Mn among the three soils. Paraquat being a positively charged herbicide will form bond with the negative charges on the hydroxyl group associated with Fe and Mn in the soil thereby reducing the population of paraquat cations in soil solution as the amount of adsorbed paraquat increased.
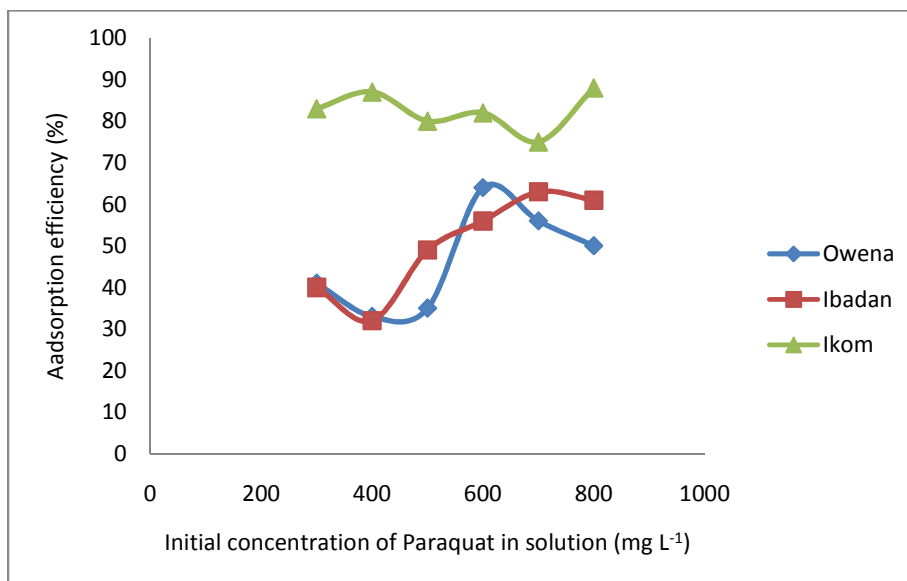

Fig. 2. Paraquat adsorption efficiency in selected cocoa soils

3.4 Langmuir Model

The Langmuir equation is widely used in many real sorption processes [29]. Its linear form is expressed as

$$\frac{ce}{x} = \frac{1}{KXmax} + \frac{c}{Xmax} \quad \text{.....................} (2)$$

Where C_e is the equilibrium concentration of paraquat ($\mu g \ ml^{-1}$) X is the quantity of paraquat sorbed per unit soil ($\mu g \ g^{-1}$), X_{max} is the adsorption maximum for a monolayer, K is the binding energy or sorption affinity.

$\frac{Ce}{X}$ versus C give a straight line from which the slope $\frac{1}{Xmax}$ and intercept $\frac{1}{(KXmax)}$ are calculated.

The values of the Langmuir constants with the correlation coefficient are listed in Table 2.

The adsorption maximum X_{max} is calculated from the reciprocal of the slope of the adsorption isotherms. This parameter reflects the number of adsorption sites available for adsorption. The sorption affinity constant K is derived from the intercept values of the isotherm. Parameter K reflects the strength with which paraquat molecules is bonded to adsorption surfaces. Result (Table 2) shows that, Ikom soil had maximum adsorption (X_{max}) of 1000 mg paraquat kg^{-1} soil while Owena and Ibadan soils had maximum adsorption of 500 and 200 mg Paraquat kg^{-1} soil respectively. The correlation coefficient R^2 obtained in Ikom soil for paraquat adsorption was higher than the R^2 values obtained in Owena and Ibadan soils. The value obtained for sorption affinity constant K was highest in Ikom and lowest in Owena soil (Table 2). This implies that, the herbicide was strongly bonded to Ikom soil compared with Owena and Ibadan soils. A similar report was given by [7] in a study of paraquat adsorption in Sri Lankan soil. They observed that, Kellale soil with high sorption maxima also had high equilibrium constant.

3.5 Freundlich Isotherm

The Freundlich isotherm is an empirical equation which estimates the adsorption intensity of the adsorbent towards the adsorbate. Freundlich equation is suitable for a highly heterogeneous surface and an adsorption isotherm lacking a plateau indicates a multilayer adsorption [30]. The model is represented by the equation

$$q = K_f \ C_e \ q^{1/n} \quad \text{...................} (3)$$

The linearized form of the adsorption isotherm was used to evaluate the sorption data and is represented as

$$\ln q = \ln K_f + 1/n \ \ln C_e, \quad \text{...................} (4)$$

where C_e is the equilibrium concentration (mg L^{-1}), q is the amount adsorbed (mg g^{-1}), K_f and n are constants incorporating parameters affecting the adsorption process, such as adsorption capacity and intensity respectively.
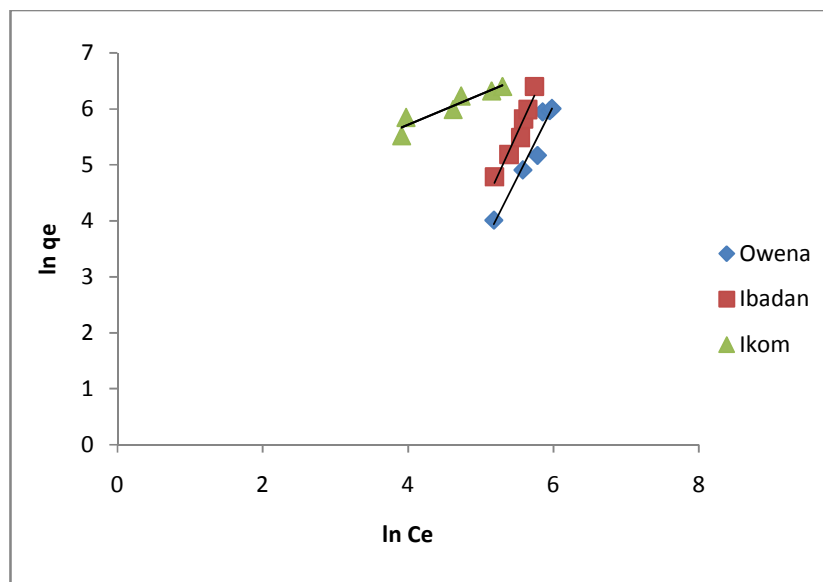
Fig. 3 shows sorption isotherms of paraquat adsorption onto the soils. In Owena and Ibadan soils, the isotherms were S- type in which 1/n > 1. The value of 1/n represents a joint measure of both the relative and diversity of energies associated with a particular sorption process. A 1/n = 1 indicates linear adsorption where equal adsorption energies for all sites exist. Linear adsorption generally occurs at very low solute concentrations and low loading of the sorbent. A value of 1/n > 1 represents S-type isotherm where the marginal sorption energy increases with increasing surface concentration. A value of 1/n < 1 represents an L-type isotherm where the marginal sorption energy decreases with increasing surface concentration. Paraquat adsorption was well described by the Freundlich model in the studied soils. The k_f value which determines adsorption capacity of each soil for the adsorbate ranged from 17.78 to 333 µmol kg^{-1} in the soils. The range of k_f values for the different soils is an indication that, soil characteristics influence adsorption capacity of soils for paraquat. Result shows that, Ikom soil had the highest K_f value due to the high clay mineral and organic matter content compared with Owena and Ibadan soils (Table 2). The positive influence of organic matter on paraquat adsorption was also reported by [31]. The linearized Freundlich equation also gave good description of paraquat adsorption in selected Sri Lankan soils as reported by [7].

The role of hydrophobic bonds in the adsorption of paraquat on organic matter within soils can be compared by normalizing the distribution coefficient K_d to the percentage of organic carbon of the various soil samples (K_{oc}). The more hydrophobic a molecule is, the higher the probability for partition from the aqueous phase to the organic phase [32]. Soil organic carbon K_{oc} can be used as a measure of such property in

Table 2. Constants obtained from Freundlich and Langmuir Isotherms

	Freundlich							Langmuir		
	OM	**K_f**	**1/n**	**R^2**	**K_d**	**K_{oc}**	**GUS**	**X_{max}**	**b**	**R^2**
Ikom	3.83	333	0.59	0.90	12.50	556	1.25	1000	0.014	0.98
Owena	3.33	61.80	1.90	0.74	6.15	332	1.48	500	0.0007	0.45
Ibadan	3.13	17.78	3.82	0.95	6.00	326	1.49	200	0.0012	0.68

Key: OM= organic matter

Fig. 3. Freundlich Isotherm of paraquat adsorption in soil

soils and it is independent of other soil characteristics. K_{oc} values should remain relatively constant if hydrophobic bonds are responsible for the adsorption of a pesticide [33]. Table 2 shows the distribution coefficient K_d and the organic carbon normalized distribution coefficient K_{oc}. The values of K_d obtained for paraquat adsorption on the studied soils ranged between 6 and 12.5 in which Ikom soil had the highest value while Ibadan soil had the lowest value. The range in K_d values suggest moderate bonding capacity of soils for paraquat. The high distribution coefficient between paraquat solution and soil surface is an indication of the affinity of paraquat for soil constituents. K_{oc} values obtained from the study ranged from 326 to 556. [34] reported K_{oc} range of 144 to 373 while [35] reported a K_{oc} range of 456 to 551. The disparity among the K_{oc} values obtained in our investigated soils suggests that paraquat adsorption in the soils was determined by some other soil properties other than soil organic

matter. This means that, soil organic matter was not the main soil constituent that determined paraquat adsorption coefficients.

Pearson correlation of soil properties and K_f in Freundlich equation showed a significant positive relationship between clay content of the soils and paraquat adsorption capacities of the studied soils (Table 3). To further evaluate the influence of soil characteristics on paraquat adsorption, the stepwise multiple regression analysis was applied which showed that, aluminium and clay minerals were the significant variables that predicted adsorption capacity of paraquat in the studied soils. Aluminium oxide alone accounted for 62.8% of the variability. When clay was added, the resulting multiple regression equation gave an increase of 31.4%. Despite the fact that, soil organic and amino acids possess negative charges which could form chemical bond with the cationic paraquat, the contribution from organic matter towards paraquat adsorption in the

studied soils was not as significant as the contribution from clay minerals. Thus, adsorption of paraquat is primarily a property of clay minerals, and the presence of expanding lattice minerals is of particular importance. A study carried out by [36] indicated that paraquat adsorption by the soil organic fraction was faster than that by the clay. Possibly, surface adsorption is instantaneous while penetration into the crystal lattice of the clay is relatively slow. Ultimately, all the paraquat ends up in the clay lattice. According to Burns and Audus, Paraquat adsorbed into the interstices of the clay particle is completely unavailable to microbial attack while the paraquat reversibly adsorbed on the surface of the organic colloid particles during the early transfer stages can be degraded [33]

Table 3. Correlation between Freundlich constants and soil properties

	K_f	n
Ca	-0.414ns	-0.076ns
Mg	0.894ns	-0.999*
Na	0.961ns	-0.709ns
K	-0.962ns	0.711ns
Al	0.997*	-0.910ns
Fe	0.983ns	-0.773ns
Mn	0.947ns	-0.675ns
pH	-0.981ns	0.765ns
C	0.987ns	-0.942ns
CEC	-0.118ns	-0.375ns
Sand	-0.997*	0.837ns
Silt	-0.717ns	0.292ns
Clay	0.992*	0.808ns

*Key: ns=not significant; * = significant at p < 0.05*

3.6 Groundwater Ubiquity Score

The groundwater Ubiquity Score (GUS) equation was used to assess the leaching potential of paraquat in the studied soils. Using half life ($t_{1/2}$) of ten years for paraquat in the soils, the groundwater ubiquity score ranged from 1.25 to 1.49 (Table 2) in which soil sample obtained from Ikom had the highest GUS value while Ibadan soil had the lowest value. Based on the classification used by [37], GUS > 2.8 is classified as leacher; 2.8 > GUS < 1.8 as transition and GUS < 1.8 as non leacher. Based on the GUS values obtained from the adsorption data, the various soils considered in this study are non leacher.

The non-leaching of paraquat in the studied soils is a function of the nature of the herbicide and the physicochemical properties of the soils. The distribution of an organic solute between sorbent and solvent phases results from its relative affinity for each phase, which in turn relates to the nature of forces which exist between molecules of the solute and those of the solvent as well as the physicochemical features of the sorbate [38].

According to [39], there are three loosely defined categories of interactions between solute and sorbent. They are physical, chemical and electrostatic. The physical sorption involves interaction between dipole moments of sorbate and sorbent molecules, chemical interaction involve covalent bond and hydrogen bond while electrostatic interaction involves ion-ion and ion-dipole forces. The environmental implication of the low GUS values obtained for Ikom, Owena and Ibadan soils is that, the use of paraquat in the control of weeds may not cause underground water contamination due to the low infiltration potential of paraquat in the soils.

3.7 Pseudo First-order Kinetics

The differential equation of pseudo first – order equation is generally expressed as

$$\frac{dq_t}{dt} = K_1(q_e - q_t) \quad \text{...............................} \quad (5)$$

Where q_e and q_t are the adsorption capacities at equilibrium and at time t, respectively in mg g^{-1}, K_1 is the rate constant of Pseudo first order adsorption (L min^{-1}). Integrating equation above for the boundary conditions t = 0 to t and qt = 0 to qt gives

$$\text{Log } (q_e - q_t) = \log (q_e) = \frac{K_1}{2.303} t \quad \text{................} \quad (6)$$

Where q_e and q_t (mg g^{-1}) are the adsorption capacities at equilibrium and at time t (h), respectively. In order to obtain the rate constants, the values of log (q_e- q_t) were linearly correlated with *t* from which K_1 and predicted q_e were determined from the slope and intercept of the plot respectively.

The pseudo-first order kinetics assumes that, the variation in adsorption rate should be proportional to the first power of concentration for strict surface adsorption. However, the relationship between initial solute concentration and the rate of adsorption will not be linear when

pore diffusion limits the adsorption process [40]. Table 3 shows that, the predicted q_e calculated from the plot ranged from 22 to 29.51, K_1 ranged from 0.4 to 0.5 while the coefficient of determination (R^2) ranged from 0.26 to 0.92. The pseudo – first order plots (not shown) suggests that application of the equation was inappropriate as experimental observations were non linear when plotted in this manner leading to low R^2 values.

3.8 Pseudo Second-order Kinetics

The pseudo-second order kinetic model which is based on the assumption that chemisorption is the rate-determining step can be expressed as:

$$\frac{t}{qt} = \frac{1}{K_2 q^2 e} + \frac{t}{q_e} \dots\dots\dots\dots\dots\dots\dots (7)$$

Where K_2 is the rate constant for pseudo-second order adsorption (g mg^{-1} m^{-1}) while t is the contact time (min) q_e is the predicted adsorbed paraquat (mg g^{-1}) and q_t (mg g^{-1}) is the amount of paraquat adsorbed at equilibrium at any time t.

This model assumes that one paraquat ion is sorbed onto two sorption sites on the soil surface. If pseudo-second order is applicable, the plot of t/q_t versus t should give a linear relationship from which q_e and K can be determined from the slope and intercept of the plot respectively. The plot of t/qt versus t is shown in Fig. 4 while the respective constants are presented in Table 4. The constant K ranged from 0.003 to 0.011. Soil obtained from Ibadan had the highest K value while Ikom soil had the lowest value. The coefficient of determination R^2 ranged from 0.83 to 0.93.

The R^2 values obtained with pseudo second order kinetics in the studied soils are much higher than the values obtained with first-order kinetics. This suggests that, second order kinetics gave better fits in describing paraquat sorption in the studied soils than the first-order kinetics. This suggests that paraquat sorbed onto the soil surface via chemical interaction. Our result is in agreement with the findings of [41].

Table 4. Calculated constants from various kinetic models

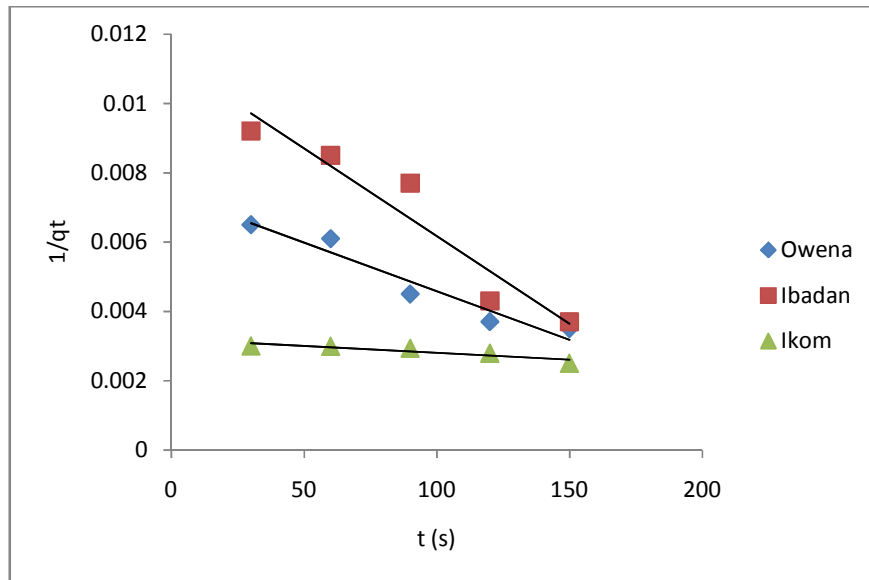| Location	Pseudo 1st order			Mass transfer			Pseudo 2nd order			Intra-particle diffusion		
	q_e	K_1	R^2	D	K_o	R^2	K	q_e	R^2	a	K_{id}	R^2
Owena	29.00	0.5	0.92	125	0.17	0.95	0.007	0.5	0.93	37.41	2.03	0.96
Ibadan	29.51	0.5	0.26	75	0.25	0.89	0.011	0.005	0.92	44.23	1.60	0.87
Ikom	22.00	0.4	0.53	317	0.029	0.94	0.003	0.06	0.83	10.07	2.50	0.96

Fig. 4. Pseudo second order kinetics equation plot

3.9 The Mass Transfer Model

The mass transfer kinetic model was used to describe the adsorption of paraquat in the evaluated soils. The equation can be written as

$$C_o - C_t = D \exp (K_o t)\ldots\ldots\ldots\ldots\ldots \ldots\text{.}(8)$$

Where

C_o is the initial paraquat concentration at time t, t is the equilibrium time (min), D is the fitting parameter, K_o is a constant relating to the mass transfer adsorption coefficient. A linearized form of the equation is:

$$\ln (C_o - C_t) = \ln D + K_o t\ldots\ldots\ldots\ldots\ldots\ldots\text{.}(9)$$

A plot of $\ln (C_o - C_t)$ versus t gave a linear relationship where $\ln D$ and K_o were determined from the intercept and slope respectively (Fig. 5).

Result (Table 4) shows that, the fitting parameter (D) ranged from 75 to 317. Ikom soil had the highest D value while Ibadan soil had the lowest value. The correlation coefficient (R^2) ranged between 0.89 and 0.95 which suggests that between 89 and 95% of the adsorption was controlled by mass transfer. Mass transfer is the movement of a chemical species in a fluid mixture caused by some forms of driving force. There are two main mechanisms of mass transfer: Diffusion and mass transport by convection. However, the rate of diffusion of ions between soil solution and soil surfaces is generally low due to molecular collisions that give rise to extremely strong hindrance to the movement of molecules.

3.10 Intra-particle Diffusion Model

The Intra-particle model, according to [42] is expressed as

$$R = K_{id} (t)a\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(10)$$

A linearized form of the equation is

$$\log q_t = \log K_{id} + 0.5 \log t\ldots\ldots\ldots\ldots\ldots(11)$$

Where

q_t is the amount of paraquat ions adsorbed at time t (mg g^{-1}), t is the contact time (min)

The model is based on the assumption that, diffusion into the interior pores of the soil particles from the soil solution controls the adsorption of paraquat ion onto the studied soils.
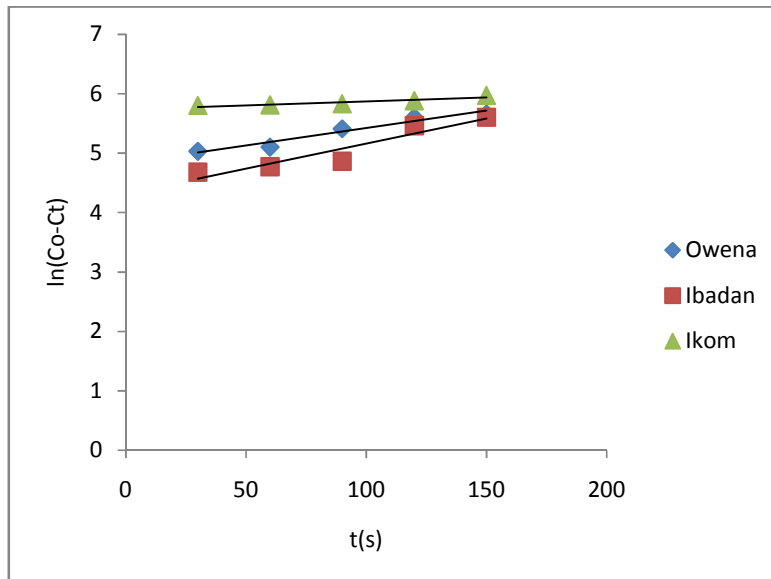

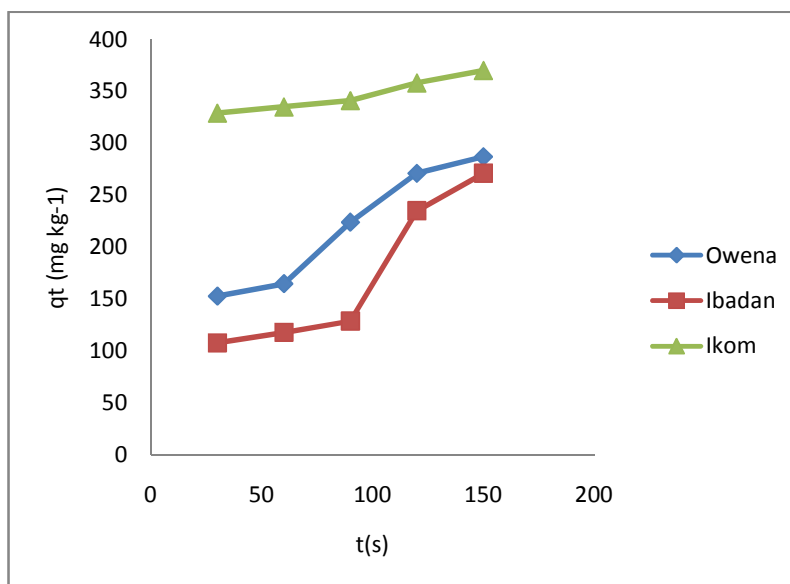**Fig. 5. Mass transfer of paraquat in soil**

Fig. 6. Intra-particle diffusion of paraquat in soil

An understanding of adsorption mechanisms facilitates the determination of the rate-limiting step. The overall rate of adsorption can be described by the following three steps: (1) film or surface diffusion, where the sorbate is transported from the bulk solution to the external surface of sorbent, (2) intra-particle or pore diffusion, where sorbate molecules move into the interior sites of the sorbent particles, and (3) adsorption on the interior sites of the sorbent [43]. Since the adsorption step is very rapid, it is assumed that it does not influence the overall kinetics. Therefore, the overall rate of adsorption process will be controlled by either surface diffusion or intra-particle diffusion. The Weber-Moris intra-particle diffusion model has often been used to determine if intra-particle diffusion is the rate-limiting step [44,45]. According to this model, a plot of qt versus $t^{0.5}$ should be linear if intra-particle diffusion is involved in the sorption process and if the plot passes through the origin then, intra-particle diffusion is the sole rate-limiting step [46]. Result (Table 4) shows that, the intra-particle diffusion rate constant K_{id} ranged from 1.60 to 2.50. This suggest that, intra-particle diffusion of paraquat ions from the soil solution onto the soil surfaces was highest in soil obtained from Ikom and lowest in soil from Ibadan. The plot of the graph obtained in the study did not pass through the origin which suggests that, intra-particle diffusion was not the sole rate - limiting step. It has also been suggested that in instances when q_t versus $t^{0.5}$ gives multi-linear plots, it means two or more

steps govern the adsorption process [47,48]. Result (Fig. 6) indicated multi-linear three steps in the plot of q_t versus $t^{0.5}$ for Ibadan and Owena while multi-linear two steps occurred in Ikom soil. The first sharper portion was the external surface or film diffusion, the second was a gradual/linear adsorption where intra-particle or pore diffusion was rate limiting and the third portion was the final equilibrium stage where intra-particle diffusion starts to slow down due to extremely low adsorbate concentration in the solution. As the plot did not pass through the origin, intra-particle diffusion was not the only rate-limiting step rather, there were three processes controlling the adsorption rate but only one was rate limiting in any particular time range. According to [49], the deviation from origin may be due to variation of mass transfer in the initial and final stages of adsorption while [50] were of the opinion that, the deviation of the plot from origin was indicative of pore diffusion being the only controlling step and not the film diffusion.

4. CONCLUSION

The study showed that, adsorption of paraquat in the investigated soils was better described by the Freundlich model than Langmuir model. The high aluminium oxides and clay contents of Ikom soil gave it an edge over Owena and Ibadan soils in the retention of paraquat within the soil matrix. This is due to the fact that, aluminium and clay were the major soil constituents that determined

paraquat adsorption. Maximum adsorption capacity (X_{max}), distribution coefficient (K_d) and sorption capacity (K_f) of paraquat in the studied soils were in a a decreasing order of Ikom > Owena > Ibadan. The groundwater ubiquity score showed that, the three soils considered in the study are non leachers of paraquat which implies that, the use of paraquat in weed control on the soils may not cause underground water contamination as the soil constituents are capable of minimizing the infiltration of the herbicide. However, infiltration of paraquat will be lowest in Ikom soil and highest in Ibadan soil due to the differences in their physicochemical properties.

COMPETING INTERESTS

Authors declare that there are no competing interests.

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