

MIGRATION OF PARAQUAT DICHLORIDE THROUGH A SANDY-LOAM SOIL

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ABSTRACT

Herbicide (paraquat dichloride) application during agricultural activity has been found to have negative consequences for humans and the environment. The soils collected from FUTO Owerri, Imo State, Nigeria were subjected to comparative investigations and analyses. A modeling approach was created in this article to mimic the pollutant (paraquat dichloride) migration process through a sandy-loam soil. The two-site parallel inter-phase model is used in this approach to simulate the soil transport process. A soil auger was used to collect soil samples at a specific location. For the experiment, a 40cm x 10cm soil column was utilized with a determined amount of 50ml of 0.5mol/L paraquat dichloride solution. The samples were divided into two categories: uncontaminated and contaminated. According to the findings, contaminated soil had the highest TOC (1.84), low conductivity (70NS/cm), low porosity (46%), and PH value (4.8), while uncontaminated soil had the lowest TOC (1.04), high conductivity (2000NS/cm), high porosity (48%), and PH value (4.8). As time passes, the effluent concentration in the soil column experiment decreases (0.0117mol/l – 0.0115mol/l) and reaches equilibrium (0.113mol/l – 0.113mol/l) between 15 and 20 minutes. The model results in this study are similar to the experimental results.

1.0 INTRODUCTION

Soil is the ultimate sink for many contaminants especially the most persistent such as chemical contaminants and organic pollutants where they may persist for many years (Aroke et al., 2013). Fomenky et al. (2018) defined Soil as the top layer of the earth's crust, formed by mineral particles, organic matter, water, air, and living organisms and it is the interface between earth, air, and water and hosts most of the biosphere. According to Totsche et al.,(2018), it is an extremely complex and variable medium; a typical sample of mineral soil comprises 45% minerals, 25% water, 25% air, and 5% organic matter; however, these proportions may vary.

The society has created a large number of chemical substances that often find their way into the environment intentionally applied during agricultural practices. Many of these chemicals represent a significant health risk when they enter the food chain and migrate down to contaminate ground water. According to Deryabin et al. (2018), contamination of both surface and ground water supplies has become a major environmental issue, particularly with the ever increasing demand for resources development and excessive usage of organic contaminants (fertilizers, herbicides) in various agricultural activities, contamination is a great concern to mankind (Kumar et al., 2005; Miribagheri, 2004). Barbaet al. (2020) pointed that

contaminants in soils and water can detrimentally impact on ecological health and human well being, such situation needs monitoring of the chemical or contaminant present in soils and the migration through it. Modeling of different kinds of contaminant was studied by several researchers and have employed mathematical and computer models (Stefianak et al 2017; Sgroi et al., 2018; James et al., 2020; Vieira et al., 2021). to study contamination of contaminant through soil mass. Inputs parameters of these models are obtained by conducting laboratory soil column test (Mirbagberi, 2004; Kumar and Sinah, 2005; Beibei et.al., 2011,) wherein soils are collected from a location along the length of the soil column to determine the effluent concentrations profile of the contaminant present.

Paraquat dichloride or I, 1-Dimethyl -4,4'- biPyridinium dichloride (systematic name), also known as methyl viologen, is an organic compound with the chemical formula $(C_6H_7N)_2 Cl_2$. (USEPA). Paraquat dichloride is a well-known herbicides which most widely used and over agricultural area in Nigeria. Paraquat dichloride is used for various applications including to control plant weeds, grasses and as harvest aid desiccants on crops such as cotton (Keachanh et al., 2018). Paraquat dichloride is available in the market, easy to access. According to US EPA and Sondhia (2014), paraquat in soil is very persistent if present in its original form, it binds strongly to both clay soil and organic matter most strongly adsorbed by clay particles (US EPA).

Many adverse health effects and environmental impacts such as lungs failure, kidney failure, affecting vital organs and blood vessels, burns in the esophagus etc have resulted from paraquat dichloride exposure. Wongwicht, D.et al., 2012 pointed that paraquat dichloride not only kills weeds but also contaminates water, soil and air as well as damages the surrounding environment, human and living organisms for maintaining ecosystem.

Paraquat dichloride is highly toxic to human and can remain active in the environment for a period of time, potentially causing acute poisoning and death after human exposure in high amount of it (D. Keachanh et al., 2018). Pesticides are categorized into four main categories which are herbicides, fungicides, insecticides and rodenticides. Herbicides are considered as the most widely used form of agricultural chemicals. There residue is the remaining on or in soil after herbicide is applied on agricultural soil. US Environmental protection agency noted that the use of Herbicide are potentially toxic to human and animals, excess of it causes soil contamination and leave Herbicide residual in the soil. Herbicides are pesticides that kill unwanted plants and weeds and are commonly used in agricultural production system throughout the world. When Herbicide is absorbed by crops, it will leach below root zone by rain or irrigation. The composition of soil is a physical factor that measures the relative amount of soil texture (sand, silt and clay) and organic, matter content of the soil. This factor affects persistence of herbicide through adsorption, leaching and volatilization (Bulu et al., 2019). Leaching of pesticides in soil was influenced by soil texture, adsorption of the pesticides on the soil particles, solubility of pesticide, volume of water flow and Ph.

In recent times, the rates at which paraquat dichloride is applied to control weeds in crop production, residential areas in urban environment has increased especially in Nigeria (Bulu et al., 2017). This application has been reported to have adverse effect on the environment. The increasing application of this herbicide could pose serious environmental problems through its migration down to ground water. In this context, numerical simulation constitute a simple,

powerful and economical approach for predicting short and long term effect of the migration of pollutant through porous soil and can be used to optimize agricultural practice while minimizing the impact on the environment. There is a definite lack of research information on the migration of Paraquat dichloride on sandy loam soil to ground water, specially addressing the amount of the contaminant that can be leached out to the ground water.

This research was done with a detailed view with application of paraquat dichloride in order to access the impact of the application or frequent use of herbicide for weed control on sandy loam soil.

2.0 MATERIALS AND METHODS

Description of study area

The study area is Federal University of Technology Owerri in Owerri West, Imo State, Nigeria. The University is bounded by the communities of Eziobodo by the south, UmuChima by the north, Ihiagwaby the west and Obinze by the east. It is a metropolitan city located between latitudes $0.5^{\circ} 38'24''$ and longitude $0.6^{\circ} 98'38''$ in the South Eastern part of Nigeria. It is characterized by sub equatorial climate with annual rainfall above 2000mm. The area experiences mean daily minimum temperature range of $19 - 24^{\circ}\text{C}$ and maximum range of $28 - 35^{\circ}\text{C}$, average relative humidity of up to 80% which lasts from April – November and a longer wet season (Mgbemena et al 2016). From the analysis, the soils are predominantly sands and little silt and clay, highly leached and acidic. The economic activities in the area due to the presence of the university are dominated by trading, subsistence agriculture, civil service and transportation.

Soil Sample Collection

Soil samples were collected using the transect method by Kumar et al. (2005). Soils were collected from a location (FUTO forest). Soil samples (replicates) were collected with a calibrated Auger from 0 – 15cm, 15cm – 30cm and 30cm – 45cm depth randomly and placed in the labeled sample bags. ie five replicates from each depth were collected for analysis. All the collected samples in the sampling bags were transported to Thermo steel Nigeria Limited in Warri delta state. Soil samples were homogenized, air dried and sieved to remove gravel, stone, plant debris and obtain aggregate that are less than 2mm in the laboratory before carrying out the analysis. The physiochemical properties were conducted.

Experimental Set up

In the laboratory, Soil Column with dimension 40cm (Length) by 10cm (Diameter) was mounted. Weighed Soil Sample of 500g was introduced into it and the soil sample occupied 30cm of the Soil Column. The Soil was moist with distilled water to allow free transport of the contaminant so as to recover the Effluent Concentration from the Soil Column. The distilled Water was allowed to drain off completely from the Column after some hours Thereafter 150ml of 0.5Mol/L of the Contaminant (Paraquat dichloride) was introduced to the moistened Soil Sample. The Effluent of the Contaminant from the Soil Column was collected at intervals of 5minutes for a total of 20 minutes study duration. The effluent was extracted with acidified methanoic acid in the ratio of 10:1 of sample to extractant, using separating funnel. The extract

was purified and 1µL of the extract was injected into the calibrated GC-MS and allowed to run. The results were recorded and tabulated as Effluent Concentration against time. See (Table.2) expressed in mol/L.

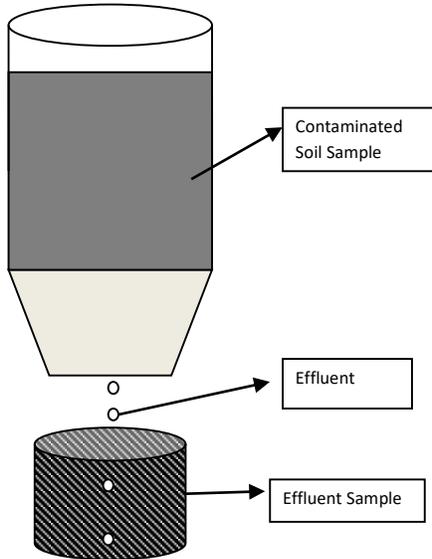


Figure 1: Experimental Set up

Analysis of the soil

The soil was also analyzed using SEM, FTIR, XRD and BET to identify the soil structure, functional group, mineral composition and surface area of the uncontaminated and contaminated soil respectively. Mineral present in the soil was identified with the help of XRD (x-ray diffraction) analysis, using an XRD-spectrometer. The presence of quartz, osumilite, garnet sepiolite, and nacrite in uncontaminated soil and the presence of quartz, orthoclase, Ilmeniteosunmilite, nacrite, and garnet in contaminated soil have been confirmed. Nova instruments were used to determine the surface area of the contaminated soil (266.97m/g). These analyses were conducted in Ahmed Bello University Zaria.

Model Description

The Model for the flow of the Contaminant through the Soil Column was given by Soon.jae et al., 2012.

Soon jae et al (2012) reported the Model for the flow of the Contaminant through the Soil Column.

Two Site Parallel Interphase (TSPI) for Type-1 and Type-2 sites that was reported by Soon.jae et al. (2012) was used to determine both equilibrium and non-equilibrium sorption parameters.

$$\frac{\partial S_2}{\partial t} = \alpha[(1 - f)KC - S_1] \quad (1)$$

Where;

C = Liquid concentration (mg/kg)

S₁, and S₂= Sorbed concentrations (mg/kg) at Type-1 and Type-2 sites,

f = fraction of the Type-1 site,

α = Sorption rate constant (h⁻¹)

K=Distribution coefficient (L/kg).

Following the sorption kinetics, the sorbed concentration (S₁) in the Type-1 site gets to equilibrium instantaneously and it satisfies the Equation below

$$S_1 = fKC_{+0} \quad (2)$$

The slow non-equilibrium sorption follows the kinetics given by Equation (1) until it satisfies this Equation.

$$S_2 = (1 - f)KC \quad (3)$$

The kinetic model [Eq. (1)] was applied to a batch system where for a given initial solute concentration (C₀) and volume (V), the total solute mass (A=VC₀) distributed in the liquid and sorbed phase remains constant. The following dimensionless forms are thus obtained.

$$S^* = S_1^* + S_2^* \quad (4)$$

$$S^* + C^* = 1 \quad (5)$$

Where; C* =C/C₀, S* =MS/VC₀, S₁ =MS₁/VC₀, and S₂ =MS₂/VC₀.

The relationship between S* and C* can be given from the Equation below:

$$S_1^* = (R\beta - 1)C^* \quad (6)$$

S₂ can also be expressed in terms of C* as follows:

$$\frac{\partial S_2^*}{\partial t} = -R\beta \frac{\partial C^*}{\partial t} \quad (7)$$

Where; R = 1 +MK/V, b = (V+ MfK)/(V+MK), fMK/V=Rb - 1, and f = (bR - 1)/(R - 1). Time-dependent sorption kinetics [Eq. (1)] in the Type-2 site can be given by

$$\frac{\partial S_2^*}{\partial t} = \alpha(RC^* - 1) \quad (8)$$

From Equations (6) and (7), we obtain the following relationship:

$$\frac{\partial C^*}{\partial t} = -\frac{\alpha}{\beta} \left(C^* - \frac{1}{R} \right) \quad (9)$$

Assumptions

Assuming that the sorbed concentration (S₁) at the Type-1 site remains constant throughout the entire reaction time the analytical solution of Equation (8) is derived as follows:

$$C^* = \frac{1}{R} + \left(C_{+0}^* - \frac{1}{R} \right) e^{-\left(\frac{\alpha}{\beta}\right)t} \quad (10)$$

Where; the relative liquid concentration (C₊₀) at t= +0 can be obtained from the following relationship:

$$f = \frac{S_{1,\infty}^*}{S^*,\infty} \approx \frac{S_{1,+0}^*}{S^*,\infty} = \frac{1 - C_{+0}^*}{1 - \frac{1}{R}} \quad (11)$$

The relative liquid concentration (C_{+0}) at $t = +0$ is given as follows:

$$C_{+0}^* = 1 - f \left(1 - \frac{1}{R}\right) = 1 - \beta + \frac{1}{R} \quad (12)$$

By substituting Equation (3.23) into Equation (3.21), we obtain the following analytical solution:

$$C^* = \frac{1}{R} + (1 - \beta)e^{-\left(\frac{\alpha}{\beta}\right)t} \quad (13)$$

3.0 RESULTS AND DISCUSSION

Physiochemical properties of the uncontaminated and contaminated soil

From table 1, the uncontaminated soil porosity is 48% while the contaminated soil has a porosity of 40%. The observed decrease in porosity is due to the interaction between the paraquat dichloride and the soil sample. As reported by Sharma et al. (2017), addition of contaminant results in a decrease in pore space. Study by Dadang, et al. (2019) using paraquat dichloride shows that the higher porosity of the uncontaminated soil enables the contaminant to attach to the pores of the soil and this evidence from the SEM result of this study. In addition, increase in porosity also influenced the increment of void ratio.

| Soil | pH | Porosity (%) | Organic content (%) | CEC (meq/100g) | Permeability (m/s) | Clay (%) | Silt (%) | Sand (%) |
|----------------|------|--------------|---------------------|----------------|--------------------|----------|----------|----------|
| Uncontaminated | 4.30 | 46.00 | 1.04 | 1.42 | 0.54 | 18.07 | 4.92 | 77.01 |
| Contaminated | 4.80 | 48.00 | 1.84 | 1.56 | 0.67 | 13.50 | 1.90 | 84.60 |

Table 1 Selected properties of the soil used in the study

Concentration profile of the effluent

The concentration of the effluent from the soil column was measured as a function of time (5- 20 minute) in the course of the migration process. Figure 2 showed the concentration followed a decreasing trend with respect to time. It is an indication of the adsorption of the contaminant in the course of the migration process. Furthermore, 150ml of solution containing 0.5mol/l of the contaminant was introduced into the Soil Column thereafter time interval of 5, 10, 15 and 20 minutes, the Effluent Concentration recovered was 0.0117mol/L, 0.0115mol/L, 0.0112mol/L and 0.0112mol/L respectively, See table 2. From the plot (see figure 2 of concentration of effluent with time), it shows a downward reduction because as time progresses, more contaminant is being absorbed into the pores of the soil. It was also observed that equilibrium was reached during the time interval of 15 to 20 minutes because the soil attained a saturation point at 15

minutes. The SEM result conjoins with the findings. The data from the results of the experiment was used to run the model (XLSTAT).The model was applied to simulate the contaminant in soil column. The model was run at 10seconds. The results reveal that the model accurately predicts the effluent's behavior as

it migrates through the soil column (see Figure 4). (comparism of the model and experiment result). The simulation result also shows a decreasing trend. The simulation was a good fit for the experimental result because it produces similar set of results in terms of the effluent concentration in the migration process through the soil column. The plot of themodel result and experimental result gave a straight line with a high correlation coefficient (97%), see figure 5. This value helped to assess the accuracy of the model and it can be inferred from the results that the model gave a high level of accuracy for the experimental result. From the model, it was estimated that it will take 4days 5 hours for the contaminant to get to ground water.

Table 2: Concentration of the effluent at different time intervals

| Concentration of Effluent, Ct (Mol/L) | Time (Minutes) |
|---------------------------------------|----------------|
| 0.0117 | 5 |
| 0.0115 | 10 |
| 0.0112 | 15 |
| 0.0112 | 20 |

Figure 2 Concentration of effluent with time

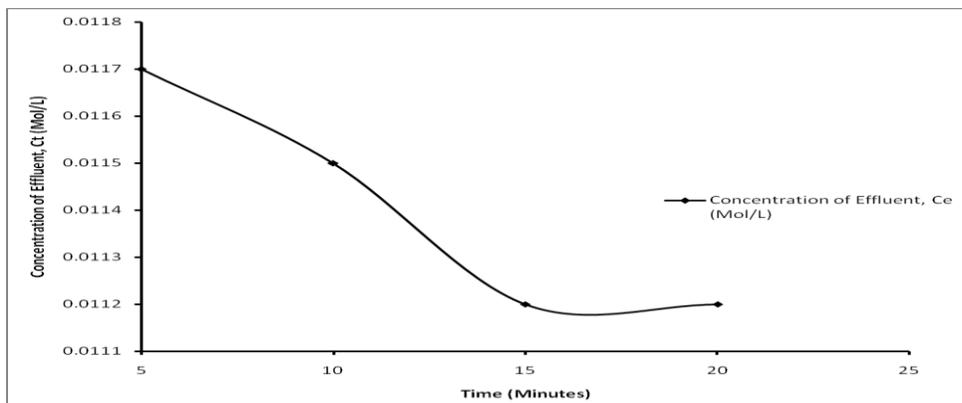


Figure 3: Model Result

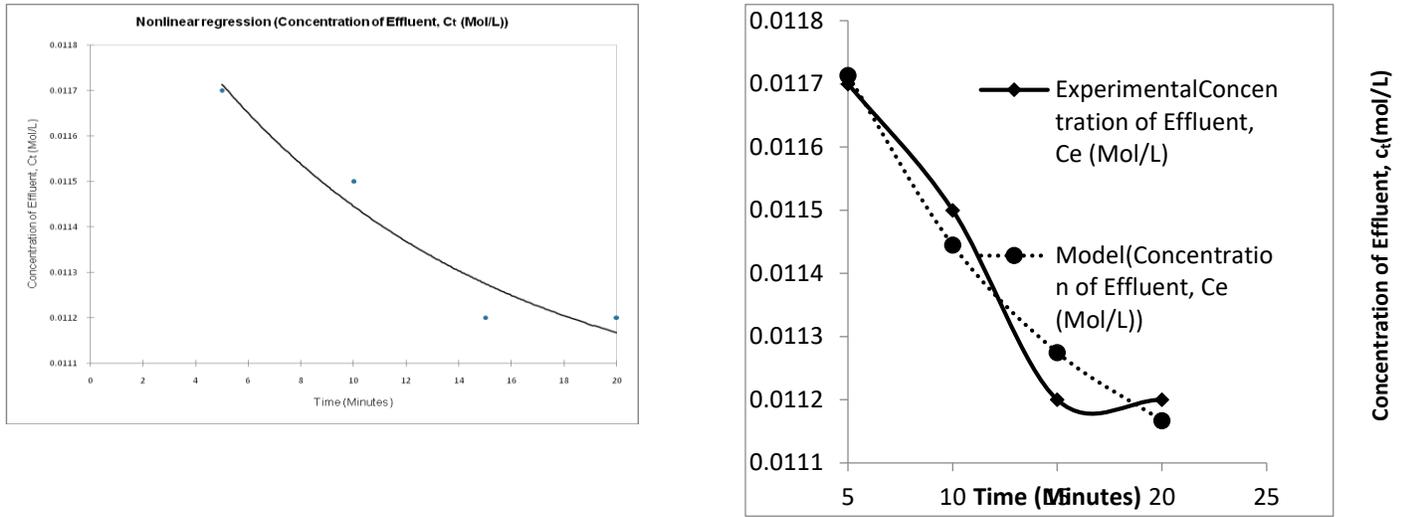


Figure 4: Comparison of the model and experimental result

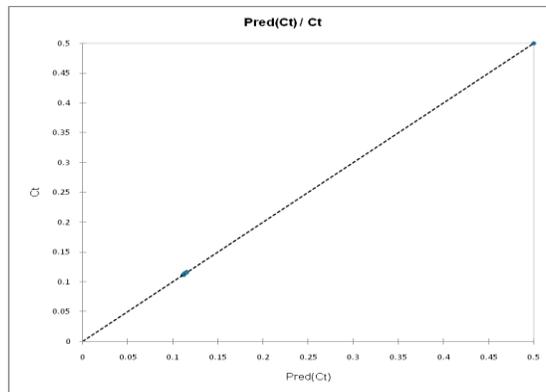


Figure 5: Plot of Model versus experimental result from the model

Xray Diffraction (XRD) Result

From the result, the uncontaminated soil sample is mainly dominated by quartz (74%) while the contaminated soil sample is also made up of mainly quartz (64%). Quartz is the most abundant minerals in most soils (Chang, et al., 2012). Report by Lee, et al. (2012) agrees to this fact. It was observed from the result that the quartz content reduced in the contaminated soil sample and this may be due to the Paraquat dichloride being polar (Janaki et al., 2015), supplies the OH functional group (as evidence from the FTIR) which reacted with the SiO_2 (Rakshit et al., 2012) and thus reduces the amount of the SiO_2 forming the Si-O-Si bond which is easily substituted by Aluminum. (Lee et al., 2012; Charles, 2016) pointed that Si undergoes isomorphous substitution by Aluminum forming a new compound.. From the result, Osumilite represents the elemental components of the uncontaminated soil with a composition of 6.5% but the Osumilite. From the result, Osumilite represents the elemental components of the uncontaminated soil with a composition of 6.5% but the Osumilite composition in the contaminated soil increases to 11% and this may be due to the Paraquat dichloride reacting with other mineral components and

liberating the metal component (Parikh et al., 2014) and this action increases the total Osumilite content in the contaminated soil (Janaki et al., 2015). The amount of Garret present in the uncontaminated soil was 2.4%. Garret is mainly made up of metal oxides (Fe, Ca, Mg) and the quantity of Garret increased in the contaminated soil which may be due to the dissociated of the OH functional group which was present in the contaminated soil reacting with different metal components to form their oxides, thus, increasing their overall presence (Njoku et al., 2016). Sepolite is the hydrated form of the Metal oxides in the uncontaminated soil sample and has the least composition (0.14%). It was observed that Sepolite was not present in the contaminated soil and this may be due to the evaporation of the water component in the uncontaminated soil in the course of the experiment due to their limited quantity (0,14%) or the absorption of the water by the Paraquat dichloride since Paraquat dichloride is hygroscopic in nature (Janaki et al., 2015) leaving only the metal oxides (Janaki et al., 2015). The contaminated soil sample contained 9% of orthoclase which was not present in the uncontaminated soil sample. The interaction between the minerals and the Paraquat dichloride liberated the Hydroxyl group which binds with the Aluminum, Potassium and Silicate (quartz) to produce orthoclase ($Al_2O_3K_2OSiO_2$). Report by (Janaki et al., 2015) also observed the presence of orthoclase.

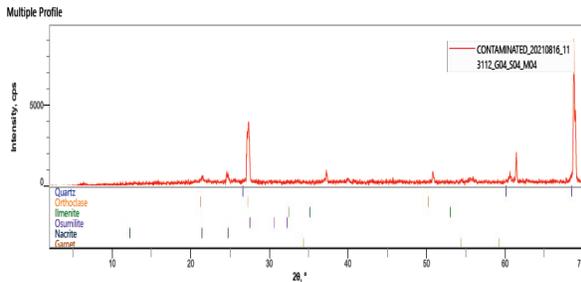


Figure 6:(a)(i) XRD Plot of the contaminated Soil Sample

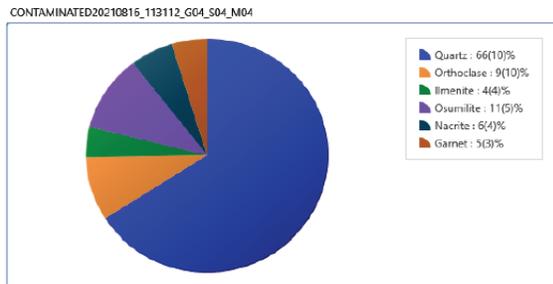


Figure 6:(b)(i) XRD Plot of the uncontaminated Soil Sample

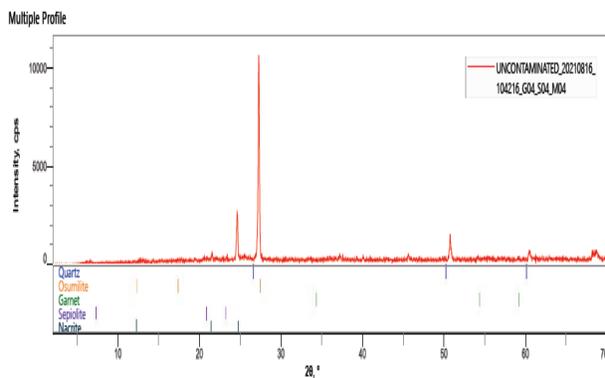
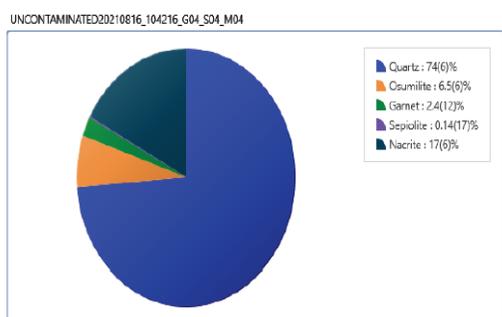


Figure 6: (b)(ii) Mineral Composition



Fourier Transform Infrared Spectroscopy (FTIR) Result

The Wave number 3649cm^{-1} observed in the uncontaminated soil (Figure 4.5a) shows Amine stretching and this slight jump in the wave number in comparison with the amine stretching (3623cm^{-1}) of the contaminated soil (Figure 4.5b) may be due to the addition of Ammonium compound from the Paraquat dichloride. Paraquat dichloride is known to contain Ammonium compound (Csernaton, 2013). The Wave number at 3395cm^{-1} of the contaminated soil (figure 4.5b) corresponds to the OH stretching (Edwards et al., 2012) functional group. This functional group causes internal vibration of the interlayer (Rakshit, et al., 2013) due to the dissociation of this group to yield Oxygen (Chang, et al., 2012; Njoku, et al., 2016) as evidence from the Ether stretch at 1028cm^{-1} (Figure 4.5b) which on further reaction, binds with the Metal element to produce their oxides (Soonjae et al., 2012). The wave number 790cm^{-1} in the contaminated soil sample was totally absent in the uncontaminated soil sample. This wave number corresponds to Alkyl halide ($-\text{C}-\text{Cl}-$) stretching. This wave number is particularly important in this study because Paraquat dichloride contains Chloride compound (Dadang et al., 2019) and the wave number is an indication of the presence of Paraquat dichloride in the Soil sample (contaminated soil).

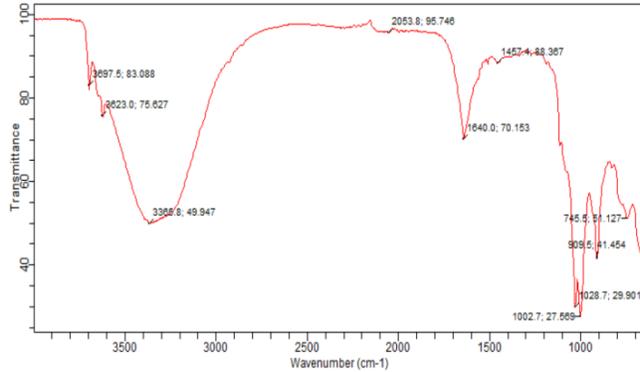


Figure7:(a)FTIR plot for the uncontaminated soil sample

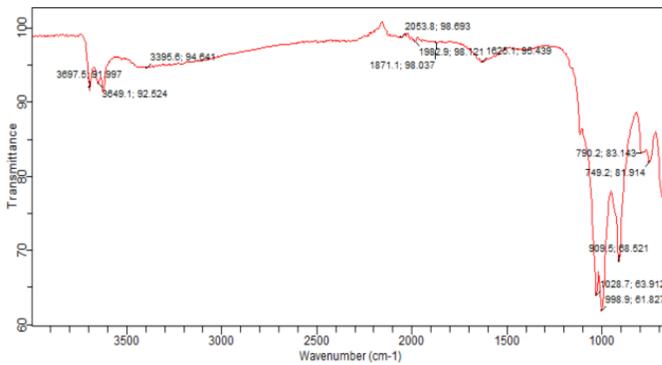


Figure 7: (b) FTIR plot for the contaminated soil sample

Scanner Electron Microscopy (SEM) Result

From the result, large pore spaces with a scattering structure were observed and this shows that the soil sample is suitable for adsorbing components. In addition (Amin, et al., 2010, suggested that there are active sites that are readily available for the adsorption process. Similar observation was also presented by Tang, et al., 2013. Figure 3 presents that the contaminant was adsorbed unto the available pores of the soil sample, thus, causing a bump like structure on each space as seen from the result. This shows that the contaminant was strongly adsorbed into the Pores of the Soil.

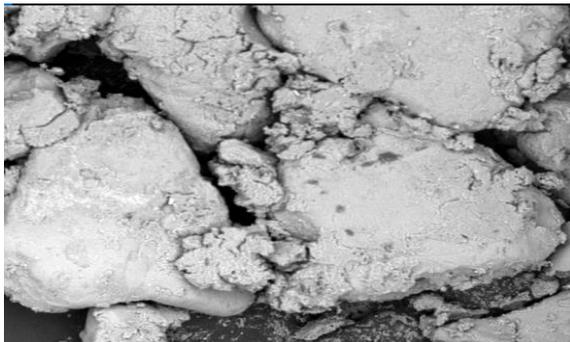


Figure 8 (a) : SEM for the contaminated (a) and uncontaminated

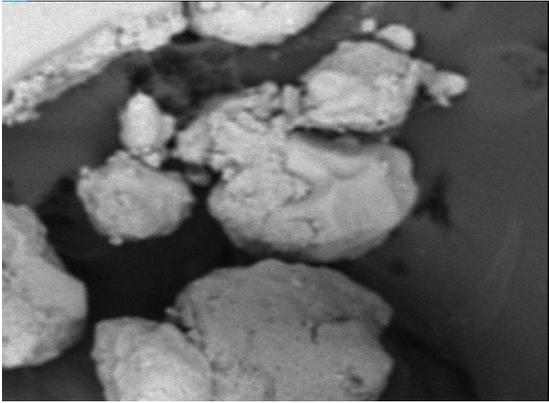


Figure 8(b) : SEM for the contaminated (b) Soil Sample

Model Validation

The model was compared against the experimental work and the accuracy of the model was determined using the Correlation coefficient value, *r*. The implication of the Correlation Coefficient is that high values say >90% gives a good fit between the experimental and model results and a low value say 80% shows a deviation of the model from the experimental result. See figure 4 and 5.

Model parameters

Table 3: Model Parameters

| Model Parameters | Value |
|-----------------------------|-------|
| β | 0.999 |
| α (t ⁻¹) | 2.39 |

For $\beta \gg 1$, It is indicative of a low permeability in the Soil that is to say, there will be a lower migration of the contaminants to the groundwater system while α represents the rate of mass transfer of the contaminant through the soil. For values of $\alpha > 1$, it indicates a slow mass transfer process. For greater α values, more space is available for the sorbed contaminant mass to diffuse inside the silt layers (zones of immobile contaminant), hence reducing the capacitance of these layers to release back the contaminant. The net effect being a reduced fraction of the contaminant-mass in the effluent consequently, a decrease in the apparent dispersivity of the mobile contaminant.

Distribution Coefficient(kd) and Retardation factor.

From the table, it shows that the distribution coefficient and retardation factor increase with time (5-10 minutes) and attained equilibrium after saturation of the Soil with the Contaminants from 15 minutes to 20 minutes. Metogbe, et al., (2018) pointed that high value of the Distribution coefficient >1 show that the Soil adsorbed more of the Contaminant, thus, there will be lesser

effluent recovery and this may be attributed to the type of Soil (Sandy-Loam) used for this study. In addition, as the distribution coefficient increases with time, it shows that the Soil gradually adsorbed the Contaminant and releases few of the Contaminant to the Root zone of the Soil. This is particularly important to ground water quality since lesser amount of the contaminant will flow into the ground water system as reported by (Dadang, et al., 2019). The retardation factors obtained in this study were greater than 1 and its implication is that the movement of the Contaminants is highly slowed down. The results help to depict the slowing down of the movement of the Contaminant to the root zone (For retardation factor greater than 1) because the higher the retardation, the lower the diffusion of the Contaminants to the root zone and subsequently limits the rate of mass transfer. Soon Jae et al. (2012) reported that the implication of this is that there will be a slow movement of the contaminant, thus, resulting to a low effluent recovery from the soil and this will have lesser impact on the ground water system

Table 4: Retardation and Distribution

| concentration of Effluent, Ct (mol/L) | Time (Minutes) | Distribution Coefficient, K_d (ml/g) | Retardation Factor |
|---------------------------------------|----------------|----------------------------------------|--------------------|
| 0.0117 | 5 | 12.52 | 17.43 |
| 0.0115 | 10 | 12.74 | 17.72 |
| 0.0112 | 15 | 13.09 | 18.18 |
| 0.0112 | 20 | 13.09 | 18.18 |

4.0 CONCLUSION

The study is an attempt to simulate pollutant transport through a soil mass. For the experimental set up, a basic and inexpensive soil column was chosen, which proved to be highly effective in detecting pollutant migration through the soil. The contaminant's introduction changed the soil's physiochemical properties. The similarities between the experimental and model results suggest that the model accurately predicts effluent concentration (behavior) as it migrates through the soil column. As the simulation goes, the effluent concentration decrease.

REFERENCES

- Amin Eisazadeh, Khairul Anuar Kassim Hadi Nur (2010). BET surface area of phosphoric acid treated tropical soils. World Congress of Soil Science, Soil Solutions for Changing World . 15-17
- Aroke, U.O, El-Nafaty U.A & Osha O.A (2013). Properties and characterization of Kaolin Clay from Alkalari, North-Eastern Nigeria. Int. J. Emerg. Technol. Adv. Eng. 3(11):387-392.
- Barba, V., Marín-Benito, J. M., Sánchez-Martín, M. J., & Rodríguez-Cruz, M. S. (2020). Transport of ¹⁴C-prosulfocarb through soil columns under different amendment,

- herbicide incubation and irrigation regimes. *Science of the Total Environment*, 701, 134542.
- Beibei, Z hou, Yanli, J., Quanju, W. and ming'an S., (2011): Chloride Transport in undisturbed soil columns of the loess Plateau. *African Journal of Agricultural Research* Vol 6, 20:PP. 4807-4815.
- Buly, yi:, Kareem, 1A and Kekere, O. (2019): soil physic chemical properties as influenced by persistent Herbicide weed control in some communities in Ondo State, Nigeria *J. Appl. Sci. Enviro) Management* Vol. 23(5): 939-945.
- Bulu, yi; Adewole, MB; and Faluyi., J.O. (2017). An analysis of adherence to precautions in herbicide application for weed control in selected cities of southwest Nigeria. *Ethiopian Journal of Environmental Studies and Management* 10 (10): 1310-1322.
- Chang, P.H., Li, Z., Jean, J.S., Jiang, W.T., Wang, C.J. & Lin, K.-H. (2012). Adsorption of tetracycline on 2:1 layered non-swelling clay mineral illite. *Applied Clay Science* 67–68, 158–163.
- Charles, L. (2016). X-Ray Diffraction And Mineralogical Analysis Of Expansive Soils In Kibaha, Tanzania. *International Journal of Engineering Inventions*, 5(8). 47-54
- Csernaton, F.; Socaciu, C.; Pop, M.R. & Bunghez, F. (2013). Application of FT-IR Spectroscopy for Fingerprinting Bioactive Molecules in a Nutraceutical PROMEN, comparatively with Plant ingredients. *J. Food Sci. Technol.*, 70, 68–69.
- Dadang, Hartono, A. Nurulalia, L., Poernomo, B. & Soekarno, W. (2019). Effects of Paraquat Dichloride application on soil Arthropods and Soil Chemical and Physical properties in Oil Palm cultivation. *J. ISSAAS* 25(2), 174-184.
- Deryabin, A. N., Unguryanu, T. N., & Buzinov, R. V. (2019). Population health risk caused by exposure to chemicals in soils. *Health Risk Analysis*, (3), 18-25.
- Edwards, H., Munshi, T., Scowen, I., Surtees, A. & Swindles, G.T., (2012). Development of oxidative sample preparation for the analysis of forensic soil samples with near-IR Raman spectroscopy. *J. Raman Spectrosc.* 43, 323–325.
- Fomenky, N.N., Tening, A.S., Chuyong, G.B., Mbene, K., Asongwe, G.A. and Che, V.B. (2018). Selected physicochemical properties and quality of soils around some rivers of Cameroon. *J. Soil Sci. Environ. Manage.*, 9(5), pp. 68-80.
- James, C. A., Lanksbury, J., Khangaonkar, T., & West, J. (2020). Evaluating exposures of bay mussels (*Mytilus trossulus*) to contaminants of emerging concern through environmental sampling and hydrodynamic modeling. *Science of the Total Environment*, 709, 136098.
- Janaki, P. & Chinnusamy, C. (2015). Field Dissiation Kinetics of Paraquat in Acid Soil as Function of Concentration and its Residues in Tea Leaves. *Asian Journal of Chemistry*; Vol. 28, No. 8, 1639-1642
- Keochanh, D., Sinlapathorn, W., Phuinthiang, P., Na Win Wattana, N., Jindakaraked, M., and Kadi Evichyanu P. (2018). Fate and transport of paraquat dichloride in corn and rubber plantation Soils. *J. Lowland Technology International* 20 (2): 125-132.
- Kumar, P.R. and Singh, D.N., (2005): A Novel Technique for monitoring Contaminant Transport through soils. *Journal of Environmental monitoring and Assessment*. 109: PP. 147-160.
- Lee, M., Woo, S. G., & Ten, L. N. (2012). Characterization of novel diesel-degrading strains *Acinetobacter haemolyticus* MJ01 and *Acinetobacter johnsonii* MJ4 isolated from oil-contaminated soil. *World Journal of Microbiology and Biotechnology*, 28(5), 2057-2067.
- Mgbemena, I. C., Ezea, C. O., Ebe, T. E., Udensi, U. J., Nwachukwu, A. A., Nzenwa, D. C., & Nwannah, A. L. (2016). Asymptomatic malaria among students of Federal University

- of Technology, Owerri (FUTO), Imo State, Nigeria. *Issues in Biological Sciences and Pharmaceutical Research*, 4(6), 50.
- Mirbagberi, S.A. (2004). Modelling Contaminant transport in soil column and ground water pollution control. *Journal of Environ Sci.* vol 1, No 2, 30:141-150.
- Nevoh, G.O, Dike, M.U and Uzoma, H.C. (2016). Physio-chemical and biological assessment of river qualities in owerri federal constituency of imo state, Nigeria. *International Journal Of Applied Research*, 2(5): 935-940.
- Njoku, M.A.; Githua, M.; Gathu, N. & Gachanja, A. (2016). Fourier transform infrared spectrophotometric analysis of functional groups found in *ricinus communis* l. and *cucurbita maxima* lam roots, stems and leaves as heavy metal adsorbents. *Int. J. Sci. Environ. Technol.*, 5, 861–871.
- Parikh, Sanjai J.; Goynes, Keith W.; Margenot, Andrew J.; Mukome, Fungai N.D.& Calderón, Francisco J. (2014) "Soil Chemical Insights Provided through Vibrational Spectroscopy" (2014). Publications from USDA-ARS / UNL Faculty.
- Rakshit, S., Elzinga, E.J., Datta, R. & Sarkar, D. (2013). In Situ Attenuated Total Reflectance Fourier-Transform Infrared Study of Oxytetracycline Sorption on Magnetite. *J. Environ. Qual.* 42, 822–827.
- Sgroi, M., Anumol, T., Roccaro, P., Vagliasindi, F. G., & Snyder, S. A. (2018). Modeling emerging contaminants breakthrough in packed bed adsorption columns by UV absorbance and fluorescing components of dissolved organic matter. *Water Research*, 145, 667-677.
- Sharma, L.D. & Sarangthem, I. (2017). Characterization of Soil Acidity and Lime Requirement in Soils of Bishnupur District, Manipur. *Trends in Biosciences* 10 (31)
- Sondihis, S (2014). Herbicides residues in soil, water, plants and non-targeted organisms and human health implications: an Indian Perspective. *Indian Journal Of Weed Science* 46 (1):66-85.
- Soonjae Lee, Dong-Ju Kim, & Jae-Woo Cho (2012). Comparison of First-Order Sorption Kinetics Using Concept of Two-Site Sorption Model. *Environmental Engineering Science*. 1002-1007
- Stefaniak, A. B., LeBouf, R. F., Yi, J., Ham, J., Nurkewicz, T., Schwegler-Berry, D. E., ... & Virji, M. A. (2017). Characterization of chemical contaminants generated by a desktop fused deposition modeling 3-dimensional Printer. *Journal Of Occupational And Environmental Hygiene*, 14(7), 540-550.
- Tang, C.S., Pei, X.J. Wang, D.Y. & Shi, B. (2013). Influencing factors on SEM images quantification of soil fabric. *Global View of Engineering Geology and the Environment – Wu & Qi (eds)*. 755-759
- Totsche, K. U., Amelung, W., Gerzabek, M. H., Guggenberger, G., Klumpp, E., Knief, C., & Kögel-Knabner, I. (2018). Microaggregates in soils. *Journal of Plant Nutrition and Soil Science*, 181(1), 104-136.
- Vieira, Y., Lima, E. C., Foletto, E. L., & Dotto, G. L. (2021). Microplastics physicochemical properties, sp interaction with pharmaceuticals and other emerging contaminants. *Science of the Total Environment*, 75
- Wongwichit, D. (2012). Risk reuaction of paraguat exposure through risk communication model in maize fa district, Nan province, Thailand
- United State Environmental Protection Agency(US EPA) Reregistration Eligibility Decision (RED) from [http:// www.epa.gov/oppsrrd](http://www.epa.gov/oppsrrd) 1/REDS/0262red.pdf.