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# Paraquat Dynamics on Western Andosolic and Ferrallitic Soils of Southern Cameroon

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## Abstract

Phytosanitary products are frequently used by agriculture worldwide and in Cameroon in particular; this with a view to protecting crops and improving agricultural yields (Riba and Silvy, 1989; Bonny, 1996; Mattews *et al.*, 2003). There are many studies on the retention of pesticides by soils, but in Cameroon, very few studies have focused on the interaction between andosols, ferralsols and the pesticides paraquat and carbendazim, which are widely used by farmers in Foumbot and Ebolowa. The objective of this work is to provide elements of understanding on the mobility of paraquat along the profile of andosolic soils of Foumbot and ferralitic soils of Ebolowa during which the soil samples were collected. The soil samples were characterized by the analytical method in accordance with the international standards at the Research Unit of Soil Analysis and Environmental Chemistry of the University of Dschang, as recommended by Pauwels *et al.* (1992). The different analyses of the soil samples were carried out according to the classical procedures of the Faculty of Agronomy and Agricultural Sciences, Soil, Plant and Water Laboratory. Statistical analysis was performed. Pearson correlation tests were performed to correlate soil physicochemical properties with soil adsorption parameters; thus, it has been observed that there is a strong correlation between the CEC and the rate of organic matter. The experimental device used for this study is a block device. This study was carried out in batch mode and by varying the contact time, the pH of the solution, the mass of the soil, the concentration of the solution. The physicochemical characterizations of the soils were studied. The mineralogical analysis was carried out by X-ray and infrared diffraction. The analysis of the samples was carried out by UV-Vis absorption spectrometry. The study of the adsorption kinetics showed that the adsorption of paraquat by the soils of Foumbot NK1, NK3 and Ebolowa MIN1 is better described by the pseudo-second order kinetic model since the $q_e$ values obtained from this model are close to the experimental values. The study of the adsorption kinetics showed that the adsorption process is very fast during the first thirty minutes and medium to very slow afterwards. The half-reaction times indicate that the kinetics of pollutant accumulation is faster on the surface of fallow soil NK1 (t1/2 = 11.30 min.), followed by cultivated soil NK3 (t1/2 = 19.94 min.) and finally the bare ground of Ebolowa MIN1 (t1/2 = 264.05 min.). Three adsorption models have been studied and the isotherms are best described by the Freundlich and Dubinin-Radushkevitch model. The adsorption of paraquat by the andosolic soils of Foumbot and the ferralitic soils of Ebolowa is best described by the Freundlich model. Bare forest soil MIN1 with a depth of 25 to 50 cm better describes adsorption with a correlation coefficient $R^2$ = 0.951 µmol/g compared to cultivated soil NK3 with a surface layer of 0 to 25 cm and finally fallows soil NK1 with a depth of 25 to 50 cm. The strong biological activity of the 25 to 50 cm deep layer of MIN1, the C/N ratio of 11.00 testifies to a good mineralization of this soil. The clay content of 45% would promote the retention of paraquat and reduce the presence of this pesticide at depth.

## Keywords

Soil, Paraquat, Depth, Retention, Kinetics, Isothermal

## 1. Introduction

Considerable quantities of pesticides have been used worldwide by intensive agriculture for more than half a century. It is estimated that 2.5 million tons of pesticides are applied to the world's crops every year [1] [2]. Since the 1950s, the intensive use of plant protection products has led to a significant increase in crop yields. Plant protection products are frequently used in Cameroonian agriculture to protect crops and improve yields [3] [4] [5] [6]. Pesticides are released into the environment during spraying and are present everywhere. Pesticide residues have been found in food. According to the latest figures for 2008, published in 2010, more than 70% of fruits and vegetables produced by intensive agriculture contain pesticide residues, with 4% exceeding the Maximum Residue Levels (MRLs); more than 60% of wheat samples and about 99% of milk samples contain pesticides. They are also present in the bodies of almost all adults and children brought there by water, air and food consumed. Organisms thus harbour hundreds of toxic molecules, including many pesticides [7] [8]. Most researchers estimate the pesticides that come into contact with or are ingested by undesirable target organisms to be less than 0.3%, which means that 99.7% of the substances spilled do not reach their target [1] [9]. Some of these toxic plant protection products are washed into surface watercourses by runoff, while the rest infiltrate and pollute groundwater [6] [10] [11] [12] [13].

Paraquat is a non-selective contact herbicide, highly soluble in water. The slow adsorption of paraquat on these soils increases its efficacy, increases its bioavailability, so it can be available to plants [14] [15], hence the need to study the behaviour of this pesticide in soils.

The objective of this research work is to provide elements of understanding on the mobility of paraquat along the profile of andosolic soils of Foumbot and ferrallitic soils of Ebolowa for a healthy and sustainable agriculture. The chemical structure of paraquat is presented in **Figure 1**.

## 2. Research Methodology

The present research work was carried out in the field for the collection of soil samples and in the laboratory for the various analyses and adsorption studies.

### 2.1. Materials

The material to be used for this research is as follows:

#### 2.1.1. Soils

- **Presentation of the study area and collection of site data**

The present study was carried out on two sites: the highlands of West Cameroon, precisely in the town of Foumbot, Nkouonke village in Noun, where andosols were sampled (the NK1 under fallow soil, the NK2 bare soil and the NK3 cultivated soil); then in South Cameroon where Ferralsols were sampled (the cultivated soil MIN2, the soil under fallow MIN3 and the bare soil MIN1). The choice of these soils is justified by the high level of agricultural activity in these areas.

#### 2.1.2. Pesticides

The pesticide paraquat, which is a herbicide, was used. The choice of this pesticide is justified by its massive use in peasant and industrial crops in Foumbot and Ebolowa.

### 2.2. Methods

#### 2.2.1. Soil Analysis Methods

The soil samples were characterised by the analytical method in accordance with the international standards in force at the Research Unit for Soil Analysis and Environmental Chemistry of the University of Dschang, as recommended by Pauwels *et al.* The different analyses of the soil samples were carried out according to the classical procedures of the soil, plant and water laboratory of the Faculty of Agronomy and Agricultural Sciences (FASA). The present research work was carried out in the field for the collection of soil samples and in the laboratory for the different analyses and adsorption studies.

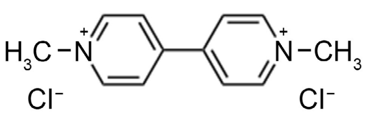



**Figure 1.** Chemical structure of paraquat.

#### 2.2.2. Soil Sampling Methods

Seven study sites representing typical characteristics of the study area and based on landscape, cropping system, organic matter composition, clay and iron content were selected. The physical and chemical properties of each site are given. After the preliminary adsorption studies, soils with low retention capacity were eliminated and only four soil samples were selected for the sorption experiments. All these soil samples were collected from the surface horizon (0 - 25 cm), crumbled, spread in a thin layer, air-dried in a ventilated area, free from contamination on plastic trays for about seven days. The samples were stirred daily to promote drying and then moderately crushed in a porcelain mortar with a porcelain pestle, without breaking up the sands and stones. The whole was sieved with a 2 mm mesh sieve and the sieve (fine soil) was kept in sealed and labelled plastic bags.

#### 2.2.3. Description of the Profile

The soil profiles of the different soil samples from Foumbot (NK1, NK2 and NK3) and Ebolowa (MIN1, MIN2 and MIN3) were produced according to the description of soil profiles proposed by the FAO (FAO, 1990). For the classification of soils, the determination of the colours of the horizons of the different profiles is done by a "Munsell" colour chart. The soil profile of Foumbot FBT located in the Foumbot Caisserie district is not included in the statistical analyses. This site was studied for simple observation.

#### 2.2.4. Collection and Preparation of Samples of the Internal Soil Horizons

The sampling and preparation of the soil samples was determined according to the methods recommended by Pauwels *et al.* The selected locations were well cleaned. Soil profiles of about 150 cm × 150 cm surface area and 150 cm depth were dug at the Nkouonke and Foumbot Caisserie sites in West Cameroon and at Minkolmingon (MIN1), Tyele (MIN2) and Mekoto (MIN3), in Central and South Cameroon. Two types of sampling were carried out:

- Sampling of the different horizons along the soil profile at different points, which consisted of collecting only those horizons that could be used to classify the soil. Soil horizons were identified by colour differences using a "Munsell" colour chart, texture, root penetration and presence of gravel. Disturbed 2 kg samples from the central part of each horizon were taken with a clean knife, starting from the lower horizons (bottom up). They were then placed in a well-labelled plastic package and transported to the laboratory.

- Collection of different depth samples along the soil profile. The aim was to study the vertical storage and mobility of substances in the soil. Disturbed samples of 2 kg depth (0 - 25 cm, 25 - 50 cm) from each profile were taken with a clean knife, starting from the lower horizons (bottom up), then put in a well labelled plastic package and transported to the laboratory.

#### 2.2.5. Collection and Preparation of Soil Surface Samples

The depth of the soil to which the plant draws water and nutrients (topsoil) depends on the depth of rooting, which in turn is determined by the plant species and edaphic constraints. Routine analysis is carried out on surface samples (0 - 25 cm). These were collected and prepared for physicochemical analysis and adsorption studies. A 2 kg mass of surface sample was hand augered three times from the Nkouonke and Foumbot Caisserie sites in West Cameroon and the Minkolmingon, Tyele and Mekoto sites in Central and South Cameroon for physicochemical analyses and adsorption studies. Twenty-five soil samples were taken according to an experimental protocol proposed by FAO. After the preliminary studies, which consisted of the first adsorption experiments, twenty-one soil samples that showed a very low adsorption rate were eliminated; only four that showed an average adsorption rate were retained for further research. The soil samples selected were mainly the surface layers with a depth of 0 to 25 cm.

## 3. Results and Discussion

### 3.1. Description of the Different Horizons of the Soil Profile

- **Soil under Nkouonke 1 (NK1) fallow**

Between (0 and 20 cm), it is an A horizon (hz A). According to the Munsell colour chart, the soil surface is Black (10YR2/1) when wet; clay-loam texture; lumpy structure with small clods of soil, easily crushed by finger pressure; friable when wet, not very plastic, not very sticky, presence of very fine pores, presence of many fine roots; presence of few channels and low biological activity; distinct and regular boundary. Between (20 and 33 cm), the AB horizon is Dark brown (10YR3/3) in a wet state; clayey-silt texture; medium to fine subangular polyhedral structure, well developed, very friable in a wet state, not very plastic, not very sticky, presence of very fine pores; medium presence of fine roots; presence of few channels and low biological activity; diffuse and regular limit. Between (33 and 54 cm), Bt horizon, Dark yellowish brown (10YR3/4) in a wet state; clayey texture; medium subangular polyhedral structure, moderately developed; friable in a wet state, not very plastic, not very sticky, presence of very fine pores. Presence of few fine roots, presence of few channels and low biological activity; distinct and wavy boundary.

- **Nkouonke 3 (NK3) cultivated soil**

Between (0 and 20 cm) is the Ap horizon. According to the Munsell colour chart, the soil surface is Dark reddish brown (5YR3/2) when dry and Dark (5YR2.5/1) when wet; the texture is clay-loam, granular structure, friable when dry, plastic and sticky when wet; not stony, presence of many fine pores; presence of many fine roots; presence of channels and common termite activity; distinct and regular boundary Between (20 and 40 cm), the BA horizon is reddish brown (5YR4/3) when dry and very dark gray (5YR3/1) when wet. Between (40 and 110 cm), the Bt horizon is yellowish red (5YR4/6) when dry and reddish brown (5YR4/4) when wet. The texture is clayey; medium subangular polyhedral structure, moderately developed; friable when dry, very sticky and very plastic when wet; not stony; presence of several very fine pores; absence of roots; presence of few channels and low biological activity.

-**Bare ground in Minkolmingon (MIN1)**

Between (0 and 8 cm), it is an A horizon (hz A). According to the Munsell colour chart, the soil surface is "Brown" (7.5YR 4/3) when wet, clayey-loamy, lumpy, sticky, plastic, many very fine to fine pores, not stony, not rocky, many fine to medium roots, intense biological activity, gradual and regular boundary. Between (8 - 34 cm), the AB horizon is "Strong brown" (7.5YR 4/6) in a wet state, clayey, medium sub-angular, sticky, plastic, many very fine to fine pores, not stony, not rocky, many medium roots, intense biological activity, presence of termite galleries, diffuse and regular boundary. Between (34 and 62 cm), horizon $B_{OX1}$ is "Strong brown" (7.5YR 4/6) in a wet state, clayey, medium sub-angular, friable (dry), very sticky, very plastic (wet), many very fine to fine pores, presence of quartz grains, many fine to medium roots, intense biological activity, presence of termite galleries, diffuse and regular limit.

### 3.2. Description of Study Sites and Classification of Soil Profiles

Description of study sites and classification of soil profiles are presented in **Table 1**.

### 3.3. Physical and Physicochemical Characteristics of the Soils Studied

**Table 2** presents the physical and physicochemical characteristics of the surface layers of the soils studied

Soil pH is the indicator of soil acidity. **Table 2** shows that after soil analysis, the results showed that the three ferrallitic soils in Ebolowa were acidic with $H_2O$ pH values between 4.2 and 5.2. The Minkolmingon soil (MIN1) was very acidic while the Tyélé (MIN2) and Mekoto (MIN3) soils were moderately acidic. The three soils at Foumbot were weakly acidic with $H_2O$ pH values ranging from 5.42 to 5.63.

Average values of organic matter (OM) were obtained in Ebolowa (3.33% and 3.95%); these values were confirmed by [16], while very high values were obtained in the soils of Foumbot, MO (3.14% and 8.61%).

The Cation Exchange Capacity (CEC) was low for the three Ebolowa soils, ranging from 7.04 to 9.92 cmol (+)/kg, and high for the four Foumbot soils: 26.02 to 36.48 cmol (+)/kg.

The Sum of Exchangeable Bases (SBE) was very low for Ebolowa soils: between 1.24 and 1.90 cmol (+)/kg and moderate for Foumbot soils: SBE between 5.36 and 8.34 cmol (+)/kg. In Foumbot, magnesium has a high value, between 3.40 and 5.68 cmol (+)/kg; this could probably be due to the cultivation history. The magnesium value is low for the Ebolowa soils, ranging from 0.40 to 0.56. Potassium, calcium and sodium values are low for all soils.

The Base Saturation Rate (BSR) was very low for the Ebolowa soils: between

13.42% and 22.30% and low for the Foumbot soils: BSR between 19.87 and 28.44 cmol (+)/kg.

### 3.4. Mineralogical Characteristics of Soils

The X-ray diffractogram of the NK1 fallow soil sample is observed at the surface horizon (0 - 25 cm) (Figure 2) as well as the IR spectra of the NK1 fallow and NK3 cultivated soils (Figure 3(a) and Figure 3(b)).

Table 1. Description of study sites and classification of representative soil profiles.

| Site characteristics | NK1 | NK3 | FBT | MIN1 |
|---|---|---|---|---|
| **Geographical coordinates** | Lat: 05˚38'73"N,<br>Length: 10˚38'899"E | Lat: 5˚37'902"N,<br>Length: 10˚39'145"E | Lat: 5˚29'918"N,<br>Length: 10˚37'354"E | Lat: 03˚17'9"N,<br>Length: 11˚33'2"E |
| **Land use/vegetation** | Soil under fallow. It is a wooded savannah at 10 m from a gallery forest colonized by *Hypparegna sp.* vegetation, which are low grasses | Soil previously cultivated by maize (*Zea mays*). | Soil previously cultivated by maize (*Zea mays*) and beans (*Phaseolus vulgaris*); soil currently populated by herbaceous vegetation Bidem spilosa Mimosa | Bare ground in the equatorial forest |
| **Soil mining**<br>- plough type<br>- type of machine<br>- fertilizer application | Under fallow | Machine | Ploughing | Uncultivated soil |
| **Geomorphology** | Flat basin. Topography of the neighbouring area is rugged and varies in altitude from 50 to 400 m | It is a bowl. | It is a bowl. | Area with a concave slope of about 3% to 4%. The surrounding vegetation is an equatorial forest zone with a herbaceous layer composed of *Chromolaena odorata* and cyperaceae |
| **Relief** | Altitude of 1145 m. | Altitude of 1 148m | Altitude of 1082 m | Altitude of 662 m |
| **Erosion/altitude** | No evidence of erosion | No evidence of erosion | No evidence of erosion | No evidence of erosion |
| **Parent materials** | Basalt | Basalt | Volcanic ash in pyroclastic deposits | Granite |
| **Soil moisture** | Aquic | Udic | Udic | Udic |
| **Soil temperature** | Isothermal | Isothermal | Isothermal | Isohyperthermal |
| **Soil classification: IUSS** working group **WRB** | Melani-Umbric Andosols (Dystric) | Melani-Umbric Andosols (Dystric) | / | Acri-Hyperdystric Ferralsol (Xanthic) |
| **Soil classification:** Soil survey staff | Typic Melanudands, medial over loamy skeletal, isothermic | Typic Melanudands, medial over loamy skeletal, isothermic | / | Kaolinitic clayey isohyperthermic Acrudox |

Table 2. Physical and physicochemical characteristics of the surface layers of the soils studied.

| N° | PROPERTIES | ANDOSOLS | | | | FERRALSOLS | | |
|---|---|---|---|---|---|---|---|---|
| | | NK1 | NK2 | NK3 | FBT | MIN1 | MIN2 | MIN3 |
| | **Texture (%)** | | | | | | | |
| 1 | Clay | 30 | 31 | 35 | 30 | 45 | 35 | 38 |
| 2 | Silt | 15 | 25 | 25 | 25 | 13 | 12 | 12 |
| 3 | Sand | 45 | 45 | 40 | 45 | 43 | 53 | 50 |
| 4 | Textural class | Sandy clay loam | Clayey Silt | Clayey Silt | Clayey Silt | Clay | Clayey Silt | Sandy clay |
| 5 | Moisture content | 3.46 | 1.76 | 1.55 | 1.03 | 0.68 | 0.59 | 0.57 |
| 6 | Bulk density (g/cm$^3$) | 0.59 | 0.79 | 0.99 | 0.53 | 1.07 | 1.27 | 1.06 |
| | **Soil reaction** | | | | | | | |
| 7 | pH KCl | 4.21 | 4.22 | 4.02 | 5.05 | 4.00 | 4.70 | 4.80 |
| 8 | pH $H_2O$ | 5.46 | 5.42 | 5.52 | 5.63 | 4.20 | 5.00 | 5.20 |
| 9 | ΔpH (pH KCl - pH $H_20$) | −1.25 | −1.20 | −1.50 | −0.58 | −0.20 | −0.30 | −0.40 |
| 10 | EC (µS/cm) | 86.30 | 106.50 | 108.50 | 62.60 | 104.30 | 116.20 | 78.10 |
| | **Organic materials** | | | | | | | |
| 11 | Total nitrogen (g/kg) | 0.24 | 0.11 | 0.14 | 0.33 | 0.20 | 0.20 | 0.17 |
| 12 | Organic Carbon (%) | 5.01 | 1.82 | 2.94 | 3.80 | 2.19 | 2.27 | 1.93 |
| 13 | Organic matter (%) | 8.61 | 3.14 | 5.07 | 6.55 | 3.78 | 3.95 | 3.33 |
| 14 | C/N ratio | 20.88 | 16.54 | 21.00 | 11.50 | 11.00 | 11.00 | 11.00 |
| | **Exchangeable cations (cmol (+)/kg)** | | | | | | | |
| 15 | Calcium | 1.88 | 1.92 | 2.32 | 1.60 | 1.04 | 1.28 | 0.72 |
| 16 | Magnesium | 5.12 | 4.32 | 5.68 | 3.40 | 0.40 | 0.56 | 0.48 |
| 17 | Potassium | 0.23 | 0.13 | 0.32 | 0.33 | 0.09 | 0.05 | 0.03 |
| 18 | Sodium | 0.02 | 0.02 | 0.02 | 0.03 | 0.04 | 0.01 | 0.01 |
| 19 | Sum of Exchangeable Bases | 7.25 | 6.39 | 8.34 | 5.36 | 1.57 | 1.90 | 1.24 |
| 20 | Exchangeable acidity ($H^+ + Al^{3+}$) | 2.52 | 2.30 | 3.58 | 0.05 | 2.10 | 0.70 | 0.55 |
| | **Cation exchange capacity (cmol (+)/kg)** | | | | | | | |
| 21 | CEC | 36.48 | 26.02 | 29.32 | 26.72 | 7.04 | 9.92 | 9.44 |
| 22 | Base Saturation Rate V (%) = S/CEC × 100 | 19.87 | 24.56 | 28.44 | 20.05 | 22.30 | 19.15 | 13.14 |
| 23 | CECE | 9.77 | 8.69 | 11.92 | 5.41 | 3.67 | 2.60 | 1.79 |

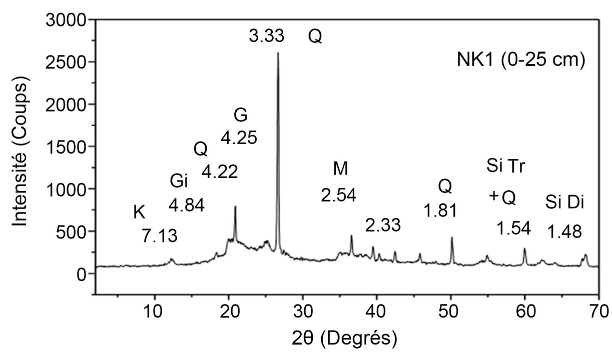
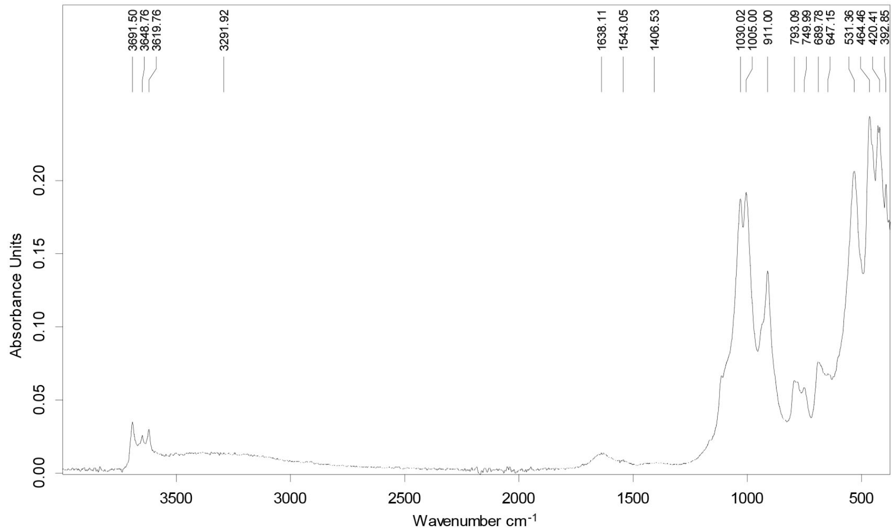
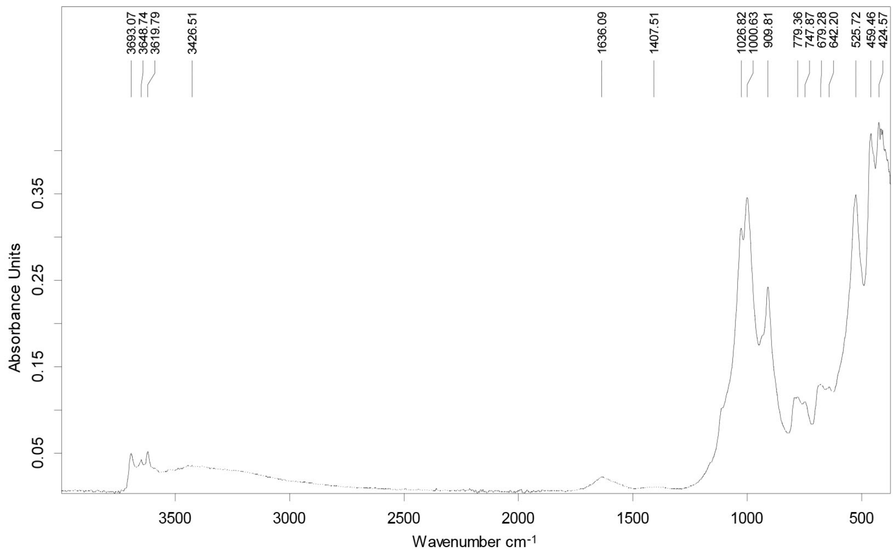



Figure 2. X-ray diffractogram of soil under NK1 fallow (0 - 25 cm). K: kaolinite, Gi: Gibbsite, G: goethite, Q: quartz, M: Magnetite, Si Tr: Trioctahedral silicates, Si Di: Dioctahedral silicates.




(a)




(b)

**Figure 3.** Infrared spectra of (a) NK1 (0 - 25 cm) and (b) NK3 (0 - 25 cm).

### 3.4.1. X-Ray Diffraction of NK1 (0 - 25 cm)

The analysis of this diffractogram shows that the dominant peaks are those of $\alpha$-quartz $SiO_2$ silica ($2\theta = 20.8˚$; $26.7˚$; $50.3˚$ and $60.1˚$). According to the literature, these distances are in agreement with those found by [2] [17]. The well-resolved peak at 12.4˚ is attributed to aluminosilicate plates containing no metallic elements, which corresponds to the kaolinite $Si_2Al_2O_5(OH)_4$ (d = 7.13 Å). According to the work of [18], some peaks corresponding to kaolinite can be observed at $2\theta = 24.9˚$ and 38.7˚ for the (002) reflection planes. Other peaks, less intense, indicate the presence of goethite ($2\theta = 21.2$). The broad diffraction peak at 33.3˚ may be from 2 phases, goethite $\alpha$-FeOOH (reflection (130)) or hematite $\alpha$-$Fe_2O_3$ (reflection (104)) [19]. Goethite, which is the free iron, is present outside the clay systems.

#### 3.4.2. Analysis of Soil Samples by IR Spectroscopy

**IR analysis of soil samples**

Figure 3(a) and Figure 3(b) show the IR spectra of the NK1 fallow and NK3 cultivated soils. Overall, it appears that the IR spectra of these different soils show the same pattern: these spectra have a very similar band distribution in the mid-infrared region for the different types of materials. This is proof that all materials have mostly identical functional groups. According to [20], these observations could explain why this technique is not sensitive enough to clearly illustrate the different types of defects in all these materials. Using the results of the literature on IR spectroscopic characterization of soils, vibrational bands have been assigned:

Some characteristic peaks can be highlighted, the presence of a broad band in the region of 3690 - 3619 $cm^{-1}$ is assigned to the stretching vibration of the internal O-H hydroxyl groups of kaolinite [21]. There are absorption bands observed around 1630 and 1400 $cm^{-1}$ in Figure 3(a) and Figure 3(b) which are attributed to the molecular O-H deformation vibration of water and the C-H elongation vibration of organic matter respectively [22]. Absorption bands around 1000 and 910 $cm^{-1}$ observed in the above mentioned figures are assigned to the Si-O elongation vibration and the Al–AlOH elongation vibration bands of kaolinite respectively. The doublet observed in the spectra of the same samples in the 745 - 790 $cm^{-1}$ region can be attributed to the intertetrahedral Si-O-Si bond of quartz [21].

#### 3.4.3. Influence of Contact Time for Paraquat Adsorption with Different Soil Samples

The study of the contact time makes it possible to determine the time required to reach the adsorption equilibrium between the adsorbent and the adsorbate. To determine this, the material and the pollutant are brought into contact for various periods of time. This time indicates the end of the adsorption process. The adsorption equilibrium reached between the soil and the pesticide will make it possible to determine the different points constituting the isotherm used. The results collected during this study are given in Figure 4.

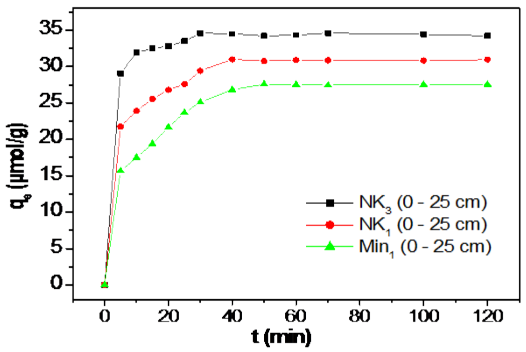



Figure 4. Influence of contact time for paraquat adsorption on NK1, NK3 and Min1 soils. Experimental conditions: 30 mg of each soil sample in 20 mL of a paraquat solution of concentration 2 × $10^{-4}$ mol/L. Stirring speed: 120 rpm at room temperature.

Analysis of these curves shows that they generally show the same pattern. The rapid adsorption of paraquat was observed during the first fifteen and twenty minutes respectively for the cultivated soil NK3 and the fallow soil NK1 until about forty minutes, which is the equilibrium time for these different soils to reach the plateau. The slope shows that there is a high affinity between the different soils and paraquat at the beginning and a saturation of adsorption sites afterwards. The NK3 cultivated soil adsorbs more and stabilizes quickly. We can say that there are two types of adsorption, one with a very steep slope and stabilizes; then the others that adsorb less and continue to adsorb. The first part characterized by a high adsorption rate is due to the fact that the number of adsorption sites initially available on the soil is high, allowing paraquat to reach them easily. The second part shows that as the contact time increases, the number of free sites on the soils decreases and the non-adsorbed molecules are assembled on the surface of the material; this limits the adsorption capacity (**Figure 4**).

#### 3.4.4. Kinetic Study of Paraquat Adsorption on NK1, NK3 and Min1 Soils

The determination of the time required to reach adsorption equilibrium requires the kinetic study of adsorption. This study also makes it possible to determine, in a comparative manner, the quantities of pesticides adsorbed as a function of time for a given initial concentration. Finally, the kinetic study of adsorption provides information on adsorption mechanisms by providing them with information. In order to study the different kinetic parameters of the adsorption of pesticides, the kinetic models of pseudo-first order, pseudo-second order and Elovich were applied to the experimental data obtained during the study of the influence of contact time on adsorption. The linear regressions relating to each of these models were plotted and the constants obtained are presented in **Table 3**.

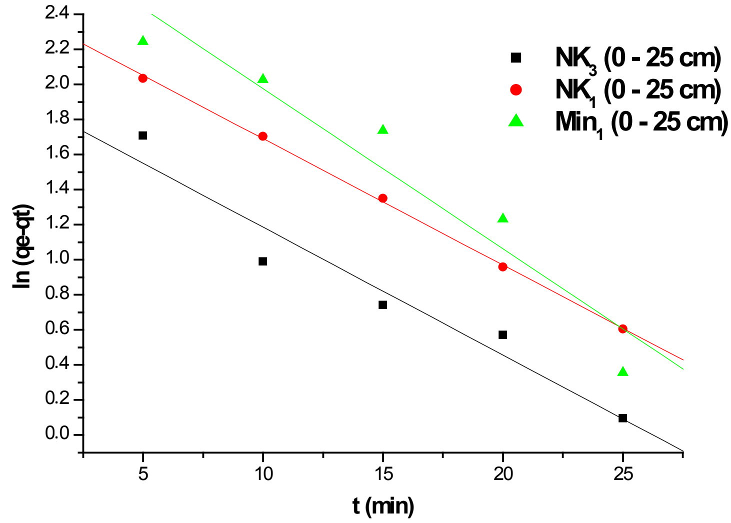
**1) Pseudo-first-order, pseudo-second-order and Elovich kinetic models**

The adsorption kinetics of paraquat by the three soils are presented in **Figures 5(a)-(c)** and the summary of the different constants obtained on the kinetic models of paraquat adsorption on the soils is presented in **Table 3**. The various adsorption kinetics were obtained for an introduced paraquat concentration of $10^{-4}$ mol·L$^{-1}$.

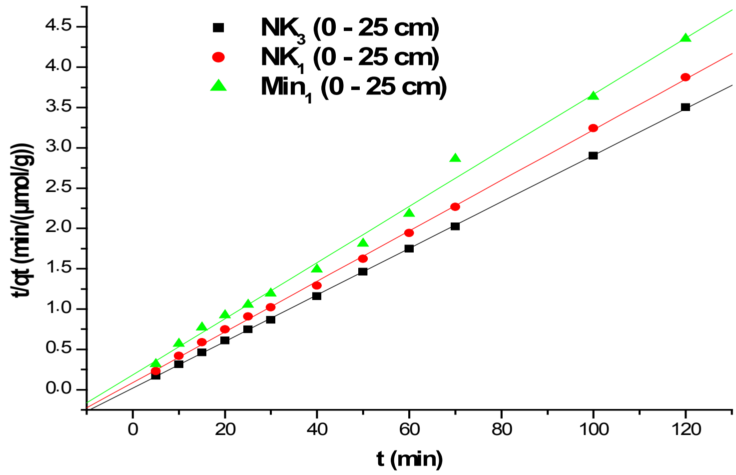
**Table 3.** Summary of the different constants obtained relating to the kinetic models of paraquat adsorption on NK1, NK3 and Min1 soils.

| Soils | Pseudo-first order | | Pseudo-second-order | | | | | | Elovich | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | $K_1$ | $R^2$ | $q_{exp}$ | $q_e$ | $K_2$ | $t_{1/2}$ | $h$ | $R^2$ | $\alpha$ | $\beta$ | $R^2$ |
| **$NK_1$ (0 - 25 cm)** | 0.072 | **0.999** | 30.990 | 31.870 | 0.111 | 11.30 | 112.740 | **0.999** | 712.300 | 0.310 | **0.898** |
| **Equations** | Y = −0.07203X + 2.41065 | | Y = 0.03137X + 0.08827 | | | | | | Y= 3.19714X + 17.28481 | | |
| **$NK_3$ (0 - 25 cm)** | 0.073 | **0.941** | 34.600 | 34.620 | 0.043 | 19.94 | 52.060 | **0.999** | 2.02E+8 | 0.660 | **0.769** |
| **Equations** | Y= −0.07289X + 1.91464 | | Y= 0.02888X + 0.0192 | | | | | | Y= 1.505556X + 28.17669 | | |
| **$Min_1$ (0 - 25 cm)** | 0.091 | **0.922** | 27.580 | 28.720 | 0.006 | 264.05 | 5.430 | **0.994** | 40.320 | 0.240 | **0.862** |
| **Equations** | Y= −0.09133X + 2.8896 | | Y= 0.03481X + 0.18377 | | | | | | Y= 4.12608X + 9.4058 | | |

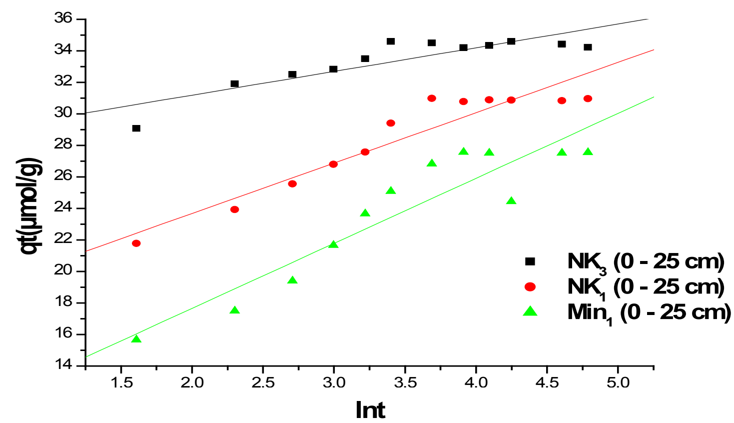
$k_1$ (min$^{-1}$), $q_e$ (µmol/g), $q_{exp}$ (µmol/g), $k_2$ (g µmol/ min), $h$ (µmol/g/min), $t_{1/2}$ (min), $\alpha$ (µmol/g/min), $\beta$ (g/µmol).




(a)




(b)




(c)

**Figure 5.** (a) Pseudo-first order kinetic study of paraquat adsorption on soils NK1, NK3 and Min1; (b) Pseudo-second-order kinetic study of paraquat adsorption on soils NK1, NK3 and Min1; (c) Kinetic study by Elovich of paraquat adsorption on soils NK1, NK3 and Min1.

**Table 3** shows that the adsorption of paraquat by the soils of Foumbot NK1, NK3 and Ebolowa MIN1 is better described by the pseudo-second order kinetic model since the $q_e$ values obtained from this model are close to the experimental values. Observation of this table shows that the correlation coefficients for this model are close to unity. This proves that this model is the most suitable for interpreting these experimental data. This observation is regular for heavy metals or for organic compounds [23] [24]. These good correlations also indicate that chemisorption is the limiting step of the process [24] [25].

The half-reaction time is the time after which half of the substance initially introduced is degraded. This time gives an indication of the persistence of the parent molecule in water, air or soil; but, it does not provide information on the metabolites. The half-reaction times indicate that the kinetics of pollutant accumulation is faster on the surface of fallow soil NK1 (t1/2 = 11.30 min.), followed by cultivated soil NK3 (t1/2 = 19.94 min.) and finally the bare ground of Ebolowa MIN1 (t1/2 = 264.05 min.). This observation shows that the soil under NK1 fallow seems more active or more available for paraquat fixation. There would be a correlation between the densities of the materials and these half-reaction times because the observation made is that they increase with the density of the materials used; which means that the diffusion of paraquat towards the fixation sites is favored in porous materials [24].

The cultivated soil NK3 adsorbs at equilibrium a quantity of paraquat of 34.620 μmol/g followed by the soil under fallow NK1 with 31.870 μmol/g and finally the bare forest soil of Ebolowa MIN1 with 28.720 μmol/g. The soils, cultivated NK3, under fallow NK1 and bare MIN1 have respective organic matter rates of 5.07%, 8.61% and 3.78%. The quantities of paraquat retained with these different soils are not all the greater when the organic matter content of the soil is high. The differences in organic matter content are not clearly reflected in the quantities retained. Organic matter does not seem to be the only factor involved in the retention of paraquat with these different soils. This classification of soils according to the importance of the quantities of paraquat retained does not make it possible to find the same classification with the rate of organic matter in the soil.

### 3.4.5. Adsorption Isotherms

The purpose of adsorption isotherms is to study the evolution of adsorption at equilibrium as a function of pesticide concentration. The isotherm curves represent the amount of pesticide adsorbed ($q_e$) as a function of the residual concentration of pesticide at equilibrium ($C_e$). In order to determine the maximum amount of pesticide that could be adsorbed onto the soil, the adsorption isotherm was performed by varying the initial pesticide concentration while keeping the other parameters constant. The adsorption isotherms of paraquat concentration $2 \times 10^{-4}$ mol·L$^{-1}$ on NK1, NK3 and Min1 soils are obtained for introduced paraquat concentrations between $10^{-4}$ and $10^{-3}$ mol·L$^{-1}$ corresponding to 3.5 to 7.0 μmol·L$^{-1}$. The contact time between soil and paraquat corresponds to the equilibrium time determined at.

**1) Modelling of paraquat adsorption isotherms**

In this research, the Langmuir, Freundlich and Dubinin-Radushkevitch (D-R) formalisms are shown in **Figures 6(a)-(c)**. These formalisms, which are widely used for the modelling of adsorption isotherms, have been used for the description of paraquat adsorption. The different parameters of **Figure 6** obtained by linearization of the equations of the three models are reported in the **Table 4**. These are the Langmuir ($K_L$, $q_{max}$), Freundlich ($K_F$, $1/n$) and Dubinin-Radushkevitch ($K$ and $E$) parameters.

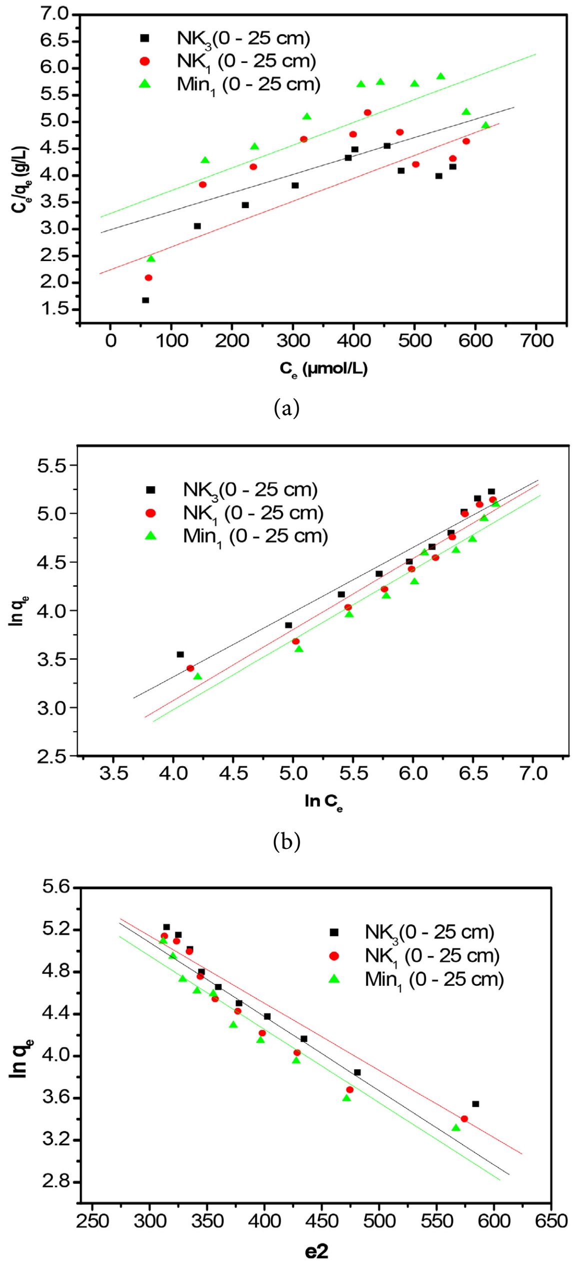



**Figure 6.** (a) Langmuir, (b) Freundlich, (c) Dubinin-R. Isotherms for paraquat adsorption on NK1, NK3 and Min1.

**Table 4.** Summary of isotherm constants for paraquat adsorption on NK1, NK3 and Min1 soils.

| Soils | Langmuir | | | Freundlich | | | Dubinin-Radushkevich | | |
|---|---|---|---|---|---|---|---|---|---|
| | $q_{max}$ | $K_L$ | $R^2$ | $1/n$ | $K_F$ | $R^2$ | $K$ | $E$ | $R^2$ |
| **NK1 (0 - 25 cm)** | 290.697 | 0.001 | **0.499** | 0.733 | 1.383 | **0.942** | 0.007 | 8.422 | **0.921** |
| **Equations** | Y = 0.00344X + 2.99133 | | | Y = 0.73248X + 0.14084 | | | Y = −0.00705X + 7.19588 | | |
| **NK3 (0 - 25 cm)** | 234.192 | 0.002 | **0.701** | 0.667 | 4.429 | **0.950** | 0.006 | 8.846 | **0.929** |
| **Equations** | Y = 0.00427X + 2.24260 | | | Y = 0.66707X + 0.64637 | | | Y = −0.00639X + 7.06094 | | |
| **MIN1 (0 - 25 cm)** | 235.294 | 0.001 | **0.596** | 0.723 | 1.216 | **0.951** | 0.007 | 8.464 | **0.935** |
| **Equations** | Y = 0.00425X + 3.29329 | | | Y = 0.72251X + 0.08494 | | | Y = −0.00698X + 7.04765 | | |

$q_{max}$ (µmol/g), $K_L$ (L/µmol), $K_F$ en (L/g), $E$ (kJ/mol), Langmuir model: $\frac{C_e}{q_e} = \frac{1}{K_L * q_{max}} + \frac{C_e}{q_{max}}$, Freundlich model: $\ln q_e = \ln K_F + \left(\frac{1}{n}\right)\ln C_e$, Dubinin - Radushkevich model: $\ln q_e = \ln X_m - K'\varepsilon^2$.

➢ **Langmuir, Freundlich and Dubinin-Radushkevitch (D-R) model**

The comparative study of the regression coefficients ($R^2$) according to Table 4 shows that paraquat adsorption isotherms for most soils are best described by the Freundlich model, followed by the Dubinin-Radushkevich model and finally the Langmuir model ($R^2$ Freundlich > $R^2$ Dubinin > $R^2$ Langmuir).

Two parameters are generated after linearization of the adsorption isotherms from the Langmuir approach: $K_L$ and $q_{max}$ representing respectively the Langmuir adsorption coefficient and the maximum adsorption quantity of the pesticide on the soil. These parameters were obtained by all soils with the line $C_e/q_e = f(C_e)$ having a positive intercept.

The maximum adsorption capacities ($q_{max}$) determined from the Langmuir formalism made it possible to classify the soils according to their performance: 290.697 µmol/g for the NK1 fallow soil, then 235.294 µmol/g for the bare soil of Ebolowa MIN1 and finally 234.192 µmol/g for the NK3 cultivated soil. According to this model, adsorption takes place on homogeneous sites and the process is favourable with the formation of a paraquat monolayer on the surface of the soils at equilibrium.

After linearization of the adsorption isotherms by the Freundlich model, two empirical parameters are generated $K_F$ and $1/n$ representing respectively the Freundlich adsorption coefficient and the affinity that exists between the pollutant molecules and the adsorption sites of the materials. The lower the value of $1/n$, the greater the heterogeneity of the sites [26]. The variability of the $1/n$ values obtained ($0.6 \le 1/n \le 1$) describing the adsorption isotherms of paraquat may reflect different distributions of adsorption sites and thus different processes involved when studying the retention of this pesticide in soil [27]. According to [2], since $1/n$ is different from 1, the isotherms are considered as non-linear in the concentration range studied (concentrations introduced at $10^{-4}$ to $10^{-3}$ mol·L$^{-1}$ corresponding to 3.5 to 7.0 µmol·L$^{-1}$). [2], after a study on the adsorption of terbumeton by soil, shows that this non-linearity has already been observed for this herbicide in a concentration range comparable to that used in this study ($0.66 \leq 1/n \leq 0.73$). According to the same author, two different types of organic matter with different structures and affinities for the pesticide may be responsible for this non-linearity at the soil level. It should be noted that, in soils, certain constituents other than organic matter (mineral constituents) participate in the retention of paraquat. Finally, since the soils studied have very different values of $1/n$ (**Table 4**) and the dimension of $K_F$ depends on this value, comparing the values of $K_F$ characterizing paraquat adsorption on different soil samples is not always a requirement.

## 4. Conclusions

The present research work has provided insights into the mobility of paraquat along the andosolic soil profile of Foumbot and the ferrallitic soil profile of Ebolowa for a healthy and sustainable agriculture.

For this purpose, the soils under NK1 fallow, NK3 cultivated and MIN1 bare were characterized by several physicochemical and spectroscopic techniques in order to obtain information concerning their composition, morphology and structure. These techniques enabled the identification of their main constituents. X-ray diffractometry analysis of these soils shows that the dominant peaks are those of $\alpha$-quartz silica $SiO_2$, kaolinite $Si_2Al_2O_5(OH)_4$, goethite $\alpha$-FeOOH or hematite $\alpha$-$Fe_2O_3$. Infrared analysis of these soils highlights the presence of the internal O-H hydroxyl groups of kaolinite, the molecular O-H groups of water, the C-H group of organic matter, the Si-O and Al-AlOH group of kaolinite; the Si-O-Si intertetrahedral bond of quartz.

Soil characteristics such as porosity, pH, CEC, clay content, etc., but above all the organic matter content, are decisive in the mobility of pesticides. The physicochemical characterisation shows that on the whole, these soils are acidic (pH between 4.2 and 5.3). The three soils studied in Ebolowa, bare soil MIN1, cultivated soil MIN2 and fallow soil MIN3, had an average organic matter with values between 3.33% and 3.95% while the four soils in Foumbot, fallow soil NK1, cultivated soil NK3, bare soil NK1 and cultivated soil FBT, had a very high organic matter between 3.14% and 8.61%. The majority of the soils had a C/N ratio of around 11 indicating well decomposed organic matter of average quality.

According to the equilibrium adsorption capacities ($q_e$) obtained, the cultivated soil NK3 ($q_e$ = 34.620 μmol/g) shows the best paraquat removal performance followed by the fallow soil NK1 ($q_e$ = 31.870 μmol/g) and finally the bare soil MIN1 ($q_e$ = 28.720 μmol/g). These observations show that the cultivated soil seems to be more active or more available for paraquat fixation, followed by the fallow soil.

The study of the adsorption kinetics showed that the adsorption of paraquat by the soils of Foumbot NK1, NK3 and Ebolowa MIN1 is better described by the pseudo-second order kinetic model since the $q_e$ values obtained from after this model are close to the experimental values. The half-reaction times indicate that the kinetics of pollutant accumulation is faster on the surface of fallow soil NK1 (t1/2 = 11.30 min.), followed by cultivated soil NK3 (t1/2 = 19.94 min.) and finally the bare ground of Ebolowa MIN1 (t1/2 = 264.05 min.). This observation shows that the soil under NK1 fallow seems more active or more available for paraquat fixation. The cultivated soil NK3 adsorbs at equilibrium a quantity of paraquat of 34.620 µmol/g followed by the soil under fallow NK1 with 31.870 µmol/g and finally the bare forest soil of Ebolowa MIN1 with 28.720 µmol/g. The soils, cultivated NK3, under fallow NK1 and bare MIN1 have respective organic matter rates of 5.07%, 8.61% and 3.78%. The quantities of paraquat retained with these different soils are not all the greater when the organic matter content of the soil is high. The differences in organic matter content are not clearly reflected in the quantities retained. Organic matter does not seem to be the only factor involved in the retention of paraquat with these different soils. This classification of soils according to the importance of the quantities of paraquat retained does not make it possible to find the same classification with the rate of organic matter in the soil.

Thus, the NK3 cultivated soil seems to be more favourable for the removal of organic pollutants. Any land use technique that influences the conservation of organic matter, CEC and clay particles on the surface can be recommended for the sustainable management of these soils. Some cultivation practices such as stirring the soil to restore its structural characteristics are recommended.

For soil remediation, organic agriculture is a production system that maintains and improves the health of soils and ecosystems.

## Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

## References

[1] Pimentel, D. (1995) Amounts of Pesticides Reaching Target Pests: Environmental Impacts and Ethics. *Journal of Agricultural and Environmental Ethics*, **8**, 17-29. https://doi.org/10.1007/BF02286399

[2] El Arfaoui, A. (2010) Etude des processus d'adsorption et de désorption de produits Phytosanitaires dans les sols calcaires. Thèse de Doctorat, Université de Reims Champagne-Ardenne, Reims.

[3] Riba, G. and Silvy, C. (1989) Combattre les ravageurs des cultures: Enjeux et perspectives. INRA, Paris.

[4] Bonny, S. (1996) Les biotechnologies en agriculture: Perspectives et enjeux. *Futuribles*, **211**, 203-215.

[5] Mattews, G., Wiles, T. and Baleguel, P. (2003) A Survey of Pesticide Application in Cameroon. *Crop Protection*, **22**, 707-714. https://doi.org/10.1016/S0261-2194(03)00008-5

[6] Tetang, T.J. and Foka, G. (2008) Utilisation des pesticides dans la zone agricole du

MOUNGO—Evaluation de l'impact sur l'environnement, la santé des populations et solutions envisageables: Cas de la localité de Njombe—Penja. Fadenah.

[7] Food and Agriculture Organization (FAO) (1978) Résidus de pesticides dans les produits alimentaires. Rapport de la réunion conjointe FAO/OMS, Rome.

[8] Générations Futures (2001) Impact des pesticides sur l'environnement et la santé. Trimestriel d'information. N˚ 43. http://www.Générations-futures.fr:Actualités

[9] ADD (2012) Alternatives Durables pour le Développement. Projet de Renforcement de la Transparence dans la Gestion des Recettes forestières annuelles dans la Commune de Dimako. GPF N˚ TF098783. Mbalmayo. http://www.alternativesdurables.org

[10] Okonkwo, J.O., Kampira, L. and Chingakule, D.D.K. (1999) Organochlorine Insecticides Residues in Human Milk: A Study of Lactating Mothers in Siphofaneni, Swaziland. *Bulletin of Environmental Contamination and Toxicology*, **63**, 243-247. https://doi.org/10.1007/s001289900972

[11] Canard, S. (2003) Devenir de l'atrazine dans l'environnement: Étude bibliographique. Thèse de Doctorat, Ecole Nationale Vétérinaire de Toulouse, Toulouse.

[12] Sansoulet, J. (2007) Transfert d'eau et des ions potassium et nitrate dans un sol à capacité d'échange anionique sous un couvert redistributeur de la pluie. Etude expérimentale et modélisation dans une bananeraie fertilisée sur un andosol. Thèse de Doctorat, Institut National Agronomique Paris-Grignon, Paris.

[13] Asian Family Support Services of Austin (AFSSA) (2008) Développement d'un indicateur d'exposition alimentaire chronique aux pesticides tenant compte des pratiques phytosanitaires en France et actualisation de la liste ORP de substances actives prioritaires. Agence française de sécurité sanitaire des aliments.

[14] Lagaly, G. (2001) Pesticide-Clay Interactions and Formulations. *Applied Clay Science*, **18**, 205-209. https://doi.org/10.1016/S0169-1317(01)00043-6

[15] Calvet, R., Barriuso, E., Bedos, C., Benoit, P., Charnay, M.P. and Coquet, Y. (2005) Les pesticides dans le sol: Conséquences agronomiques et environnementales. Editions France Agricole, Paris.

[16] Onana, A.A. (2018) Effet des amendements organiques et du phosphate diammonique (2AP) sur la libération, le recouvrement et les paramètres agronomiques du phosphore sur un sol ferrallitique typique d'Ebolowa au Sud Cameroun. Ph.D. Thesis, Université de Dschang, Dschang.

[17] Flogeac, K. (2004) Etude de la capacité de rétention de produits phytosanitaires par deux solides modèles des sols. Influence de la présence des cations métalliques. Thèse de Doctorat, Université de Reims Champagne-Ardenne, Reims.

[18] Brown, G. and Brindley, G.W. (1984) Crystal Structures of Clay Minerals and Their X-Ray Identification. 2nd Edition, Mineralogical Society, London, 305-360.

[19] Baley, S.W. (1967) Structures of Layer Silicates. *American Geological Institute*, **1**, 142 p.

[20] Madejová, J. and Komadel, P. (2001) Baseline Studies of the Clay Minerals Society Source Clays: Infrared Methods. *Clays and clay minerals*, **49**, 410-432. https://doi.org/10.1346/CCMN.2001.0490508

[21] Bertaux, J., Fröhlich, F. and Ildefonse, P. (1998) Multicomponent Analysis of FTIR Spectra: Quantification of Amorphous and Crystallized Mineral Phases in Synthetic and Natural Sediments. *Journal of Sedimentary Research*, **68**, 440-447. https://doi.org/10.2110/jsr.68.440

[22] Stenberg, B., Rossel, R.A.V., Mouazen, A.M. and Wetterlind, J. (2010) Visible and

Near Infrared Spectroscopy in Soil Science. In: Sparks, D. and du Pont, S.H., Eds., *Advances in Agronomy*, Academic Press, Cambridge, 163-215. https://doi.org/10.1016/S0065-2113(10)07005-7

[23] Febrianto, J., Kosasih, A.N., Sunarso, J., Ju, Y., Indraswati, N. and Ismadji, S. (2009) Equilibrium and Kinetic Studies in Adsorption of Heavy Metals Using Biosobent: A Summary of Recent Studies. *Journal of Hazardous Materials*, **162**, 616-645. https://doi.org/10.1016/j.jhazmat.2008.06.042

[24] Kenne, G.D. (2011) Biosorption du paraquat par des matériaux lignocellulosiques et élaboration de capteurs électrochimiques à film de sciure de bois. Thèse de Doctorat Ph.D., Université de Yaoundé I, Yaoundé.

[25] Muhamad, M., Khan, M.A. and Choong, T.S.Y. (2012) Adsorptive Separation Studies of $\beta$-Carotene from Methyl Ester Using Mesoporous Carbons Coated Monolith. *Journal of Chemistry*, **2013**, Article ID: 235836.

[26] Xing, B., Pignatello, J.J. and Gigliotti, B. (1996) Competitive Sorption between Atrazine and Other Organic Compounds in Soils and Model Sorbents. *Environmental Science & Technology*, **30**, 2432-2440. https://doi.org/10.1021/es950350z

[27] Weber, W.J., Leboeuf, E.J., Young, T.M. and Huang, W. (2001) Contaminant Interactions with Geosorbent Organic Matter: Insights Drawn from Polymer Sciences. *Water Research*, **35**, 853-868. https://doi.org/10.1016/S0043-1354(00)00339-0