

# Study of Potential Adsorption of Glyphosate on Iron-textured Soil

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**Abstract:** The main goal of this study is to evaluate the potential for glyphosate to contaminate water and ground water. For this purpose, the adsorption of glyphosate on a soil of culture in West of Côte d'Ivoire is investigated. The chemical composition of the soil, the different materials that compose it as well as the pH of zero charge of this soil were determined. The results revealed that the soil sample was rich in iron oxide mainly goethite, phengite and anatase. Adsorption kinetics was studied and the rate of sorption was found to conform to pseudo-second-order kinetics with 90 min as equilibrium time. Equilibrium isotherm data were analyzed according to Langmuir and Freundlich models. The two models describe the adsorption phenomenon well. The soil is heterogeneous with a good affinity between the metal oxides of the soil and the glyphosate. The maximum adsorption capacities were determined to be 2.68 mg/g. Parameters such as the initial pH of the solution, the mass of soil and the temperature were well investigated. It is observed that the adsorbed amount of glyphosate increases with temperature, reflecting the endothermic nature of the adsorption. The maximum amount of glyphosate adsorbed at 40°C is approximately 3 mg/g. The amount of glyphosate adsorbed increases with the initial concentration and decreases with the increase of pH. The optimal pH is therefore 5.

**Keywords:** Pesticides, Iron Oxides, Adsorption Phenomenon, Kinetics, Isotherm, pH

## 1. Introduction

Pesticides are widely used around the world. They are used to eliminate weeds, control crop pests and help preserve agricultural products. The use of these chemicals in modern farming practices is viewed as an integral part of the success of the agricultural [1]. There are many varieties of pesticides commonly classified according to the biological target as rodenticides, insecticides, larvacides, miticides (acaricides), molluscides, nematocides, repellants, synergists, fumigants, fungicides, algicides, herbicides, defoliant, desiccants, plant growth regulators and sterilants [2].

Among the herbicides, glyphosate (N-(phosphonomethyl) glycine) is an extremely effective broad spectrum herbicide manufactured by the Monsanto Company. It is a nonselective

systemic herbicide used for plants control including grasses, sedges, broad-leaved weeds, and woody plants [3]. Glyphosate is known in several commercial formulations including Roundup. It is the most widely used herbicide in the world [4-5]. Thus, it can be found strongly in the environment with variable residues and metabolites. Due to intensive use and accumulation of glyphosate in the environment, some harmful effects have been reported for plants, animals, and human health, such as weakening plant systems, disrupting the metabolism of terrestrial and aquatic animals and causing endocrine disruption to human, the International Agency for Research on Cancer classified glyphosate as "probably carcinogenic to humans", while authors disagree on this conclusion, which requires further research [6-7]. In all cases, knowing whether or not it is available in the receiving environment after use is important for the safety of the population.

The study of the adsorption of glyphosate on the soil or on soil components as well as its degradation by microorganisms are widely carried out and reported in the literature [8-9]. Thus the adsorptions of glyphosate on clay minerals [10], on ferric oxides [11], as well as its degradation by microorganisms [12] were carried out. These studies show a strong influence of the pH on the elimination of glyphosate.

The objective of this work is to study the adsorption of glyphosate on a soil with a ferrous texture. For this the soil has been characterized. We have also studied the influence of certain parameters, in particular the pH, on the adsorption phenomenon.

This study is important in order to minimize the risk of water (surface and ground) contamination for country such as Ivory Coast (Côte d'Ivoire), where glyphosate constitutes more than 50% of herbicide used in agriculture [13].

## 2. Material and Methods

### 2.1. Chemicals Reagents

The main chemical in this study is glyphosate. Glyphosate (PESTANAL®, analytical standard, supplied by Sigma-Aldrich) was used as a standard and a soluble liquid (SL) type formulation called Power 360, purchased from the company AGRITEC, dosed at 360 g/L of glyphosate (41% isopropylamine salt) per liter of commercial solution were used. Other chemicals reagents were used including acetic acid of purity 99.5%, hydrochloric acid of purity 37% purchased from Carlo Erba, sodium hydroxide (NaOH) 0.2M and sodium chloride (NaCl) for analysis supplied by Scharlau as well as ultrapure water for the study.

### 2.2. Apparatus

Many apparatus were used for the laboratory study including a pH meter (multiparameter HQ 40d), a Vibramax 100 magnetic stirrer, a UW4200H SHIMADZU balance, a SHIMADZU HPLC chain, a GBC brand DRX device Emma with a copper anticathode and a HORIBA scientific MESA-50 X-ray fluorescence device.

### 2.3. Material of Chromatography Analysis

The high performance liquid chromatography (HPLC) line used in this work is one of the Central Laboratory for Analysis and Ecotoxicology (LCAE). It is a device manufactured by the company SHIMADZU (Japan). These constituents are:

1. SIL-20A automatic injector
2. Column: Lichrospher 100 ODS (250 L x 4.6 mm);
3. Pump (isocratic method) LC-20AT;
4. SPD -20A UV absorption detector set to the
5. Data acquisition using LC-Solutions software (Shimadzu, LC-20A).

### 2.4. Soil Characterization

The pH of zero charge (pH<sub>zc</sub>) was determined in order to know the character of the soil according to the pH of the

solution. For its determination, 50 mL of NaCl solution (0.01 M) was introduced into the reactors containing 0.15 g of soil to be analyzed. The pH of each reactor is adjusted (variation of the values between 2 and 12, in steps of 1) by adding 0.1 M NaOH or HCl solution. Stirring is maintained for 48 hours using a multi-stirring system, at a temperature of 25°C. The contents of these reactors are then filtered using filter membranes with a pore diameter of 0.45 µm. The final pH of each mixture is then measured. We draw the graph  $\Delta\text{pH} = f(\text{pHi})$ , where  $\Delta\text{pH} = (\text{pHf} - \text{pHi})$ . The pH<sub>zc</sub> is defined as the point of intersection of the curve with the axis which passes through zero [14].

Energy-dispersive X-ray fluorescence was used to determine the chemical composition of the soil, as well as X-ray diffraction, to identify the essential materials in the soil sample for this study.

### 2.5. Procedure for Analysis

Sample derivatization procedure was as follows:

To 1 mL of extract is added 1 mL of sodium tetraborate solution (5%) and 1 mL of FMOC solution (10 g.L<sup>-1</sup>). The solution obtained is stirred for 1 hour then the supernatant is collected in a vial and close for detection and quantification by HPLC.

The calculation formula:

$$C_p = \frac{S_{ech} \times C_e \times F}{S_e} \quad (1)$$

Where  $C_p$  is concentration of glyphosate (mg.L<sup>-1</sup>),  $C_e$  is glyphosate standard concentration (mg/L),  $S_{ech}$  is sample peak area,  $S_e$  is peak area of the standard and  $F$  is the factor of dilution.

### 2.6. Kinetic Adsorption Study

The study of the kinetics of adsorption of glyphosate was carried out at room temperature on iron-textured soil. The aim is to determine the time required to reach equilibrium iron-textured soil adsorption and kinetic order. For kinetic adsorption study, 10 g of soil was mixed with 400 mL of 10 mg.L<sup>-1</sup> of glyphosate solution in a 500 mL conical flask. A mixture similar is done with 100 mg.L<sup>-1</sup> of glyphosate. These mixtures were shaken on magnetic agitator at 300 rpm for intervals time of 10 and 150 minutes. After each contact time solutions were filtered and the initial and final concentrations of glyphosate were determined by HPLC. The conditions used for our analysis are:

1. Injection volume of 10 µL;
2. Column: Lichrospher 100 ODS (250 L x 4.6 mm);
3. Elution mode: isocratic;
4. Eluent A: 50 Mm of ammonium acetate (40%);
5. Eluent B: acetonitrile HPLC gradient (60%);
6. Flow rate: 0.5 mL.min<sup>-1</sup>;
7. Temperature: 30°C;
8. Wavelength (λ): 254 nm.

The amount of glyphosate adsorbed onto iron-textured soil is calculated according to the following equation:

The amount of glyphosate adsorbed onto iron-textured soil is calculated according to the following equation:

$$q_t = \frac{(C_0 - C_t)}{m} \times V \quad (2)$$

Where  $q_t$  is the amount of glyphosate adsorbed by iron-textured soil ( $\text{mg.g}^{-1}$ );  $C_0$  and  $C_t$  are respectively the initial and the final concentration of glyphosate at time after filtration ( $\text{mg.L}^{-1}$ );  $V$  is the initial solution volume (L);  $m$  is the mass of the iron-textured soil (g).

## 2.7. Adsorption Isotherms

For equilibrium adsorption study, 2 g of iron-textured soil was mixed with 50 mL of different glyphosate concentrations: 25  $\text{mg.L}^{-1}$ , 40  $\text{mg.L}^{-1}$ , 50  $\text{mg.L}^{-1}$  and 75  $\text{mg.L}^{-1}$  in 100 mL conical flasks. Then reaction mixtures were shaken on magnetic agitator at 300 rpm for equilibrium time (90 min) at room temperature. After equilibrium time, samples were filtered and analyzed by HPLC under the conditions mentioned above. The amount of glyphosate adsorbed per unit mass of iron-textured soil at equilibrium,  $q_e$ , was calculated by:

$$q_e = \frac{(C_0 - C_e)}{m} \times V \quad (3)$$

Where  $C_0$  and  $C_e$  are the concentrations of glyphosate at initial and equilibrium times, respectively;  $V$  is the volume of the (L); and  $m$  is the mass of iron-textured soil used (g).

## 3. Results and Discussion

### 3.1. Soil Characteristics

#### 3.1.1. PH of Zero Charge

The  $\text{pH}_{\text{ZC}}$  is a good indicator of the chemical and electronic properties of functional groups. So when  $\text{pH}_{\text{ZC}} > \text{pH}$ , the surface of the material is positively charged, while when  $\text{pH}_{\text{ZC}} < \text{pH}$  the material surface is negatively charged [15]. The pH of zero charge of iron-textured soil is given in

Figure 1. The  $\text{pH}_{\text{ZC}}$  value is 5.4, suggesting the acidic character of the soil.

If the pH of the solution is lower than  $\text{pH}_{\text{ZC}}$ , the surface functional groups of the iron-textured soil will be protonated by an excess of  $\text{H}^+$  protons from the solution, the adsorbent is a negatively charged adsorbate attractor. On the contrary, if the pH of the solution is higher than the  $\text{pH}_{\text{ZC}}$  the functional surface groups will be deprotonated by the presence of  $\text{OH}^-$  ions in the solution, therefore the support is a positively charged adsorbate attractor [16]. Thus the adsorption of cationic molecules on this soil in aqueous medium would be favored if  $\text{pH} > 5.4$ .

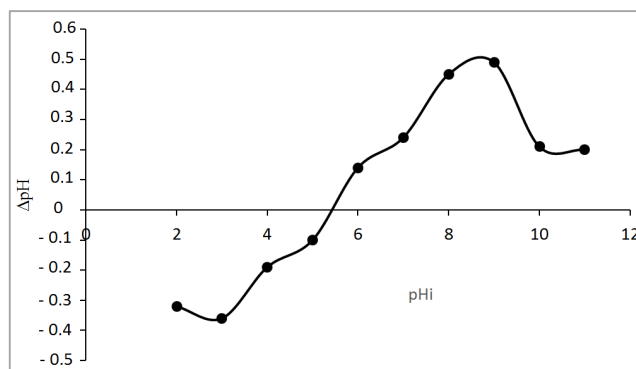


Figure 1. Curve for determining the pH of zero charge.

#### 3.1.2. Chemical Composition of the Soil

X-ray fluorescence analysis was performed on the soil of this study to determine its chemical composition. This analysis was carried out with the x-fluorescence apparatus type HORIBA scientific MESA from the University of Man. Table 1 below summarizes the content of the chemical elements present in the sample. The material used in our study consists mainly of iron oxide (48.77%) and  $\text{FeO}(\text{OH})_2$  (14.41%). Silicon oxide is present at 8.25% and alumina at 7.32%.

Table 1. Chemical composition of the soil.

Element	K <sub>2</sub> O	CaO	TiO <sub>2</sub>	V <sub>2</sub> O <sub>5</sub>	Mn <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	FeO(OH) <sub>2</sub>	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CuO	MoO <sub>3</sub>
Value	7.1343	4.8768	4.784	0.1535	0.3223	48.77	14.412	8.256	7.326	0.3223	0.2658
Element	Ag <sub>2</sub> O	As <sub>2</sub> O <sub>3</sub>	Ba	U <sub>3</sub> O <sub>8</sub>	P <sub>2</sub> O <sub>5</sub>	Au <sub>2</sub> O <sub>3</sub>	CoO	S	Sr	Zr	
Value	0.0093	0.0123	0.9082	0.0498	0	0	0	0	0.5711	0.4189	

#### 3.1.3. X-ray Diffraction

The XRD analysis was performed at the University of Man. The result of the XRD of iron-textured soil is shown in Figure 2. It is a heterogeneous material consisting mainly of: Quartz, Phengite, Goethite, Iron Hydroxide Phosphate, and Anatase. Anatase is a mineral species formed from titanium oxide ( $\text{TiO}_2$ ). Its presence is well confirmed by the result of X-ray fluorescence. Goethite is a mineral species, variety of iron (III) oxyhydroxide,  $\alpha$  polymorph of the compound  $\text{FeO}(\text{OH})$  with traces of Mn and  $\text{H}_2\text{O}$ . Its presence is also confirmed. Phengite is confirmed by the presence of  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$  and  $\text{Fe}_2\text{O}_3$ . As this material is rich in oxide and cation, it can properly adsorb organic molecules including pesticides [17-18].

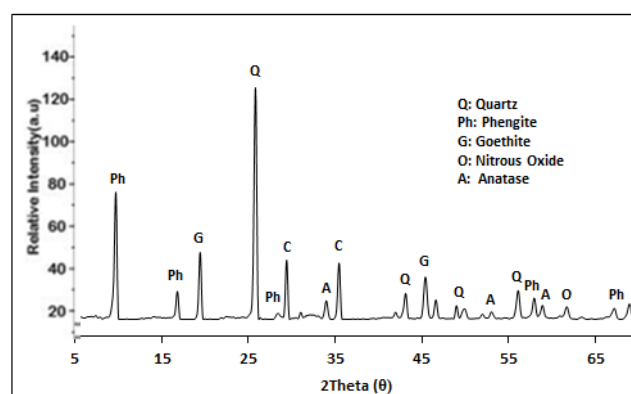


Figure 2. X-ray diffraction of soil sample.

### 3.2. Adsorption of Glyphosate

#### 3.2.1. Adsorption Kinetics

The study of the kinetics of adsorption of glyphosate on iron-textured soil was carried out at room temperature. The result is shown in figure 3. We found that the concentration of glyphosate decreases as a function of time for each of the initial concentrations (10 mg.L<sup>-1</sup> and 100 mg.L<sup>-1</sup>). This decrease in concentration is rapid during the first 30 minutes for 100 mg.L<sup>-1</sup> and decreases less rapidly up to 120 min. For the 10 mg.L<sup>-1</sup> concentration, the concentration decreases more rapidly almost similarly to that of 100 mg.L<sup>-1</sup>. These two phases in the evolution of the curve can be explained as follows: the first rapid phase corresponds to the saturation of

the pores. For this phase, the curve of 100 mg.L<sup>-1</sup> decreases more rapidly. This is due to the high concentration so more molecules to be absorbed. In the second phase, with the pores saturated, there is a migration and slow diffusion of glyphosate molecules into the soil after saturation of the vacant sites [19]. In all cases, after 120 min the residual metal concentrations vary very little, indicating saturation of the pores of the iron-textured soil. A time of 90 min will therefore be used as the equilibrium time for the study of all the isotherms. The adsorption of glyphosate on 3 Chilean soils gave the same equilibrium time of 90 min as well as the adsorption of glyphosate on activated carbon based on the bark of *Eucalyptus camaldulensis* [5-20].

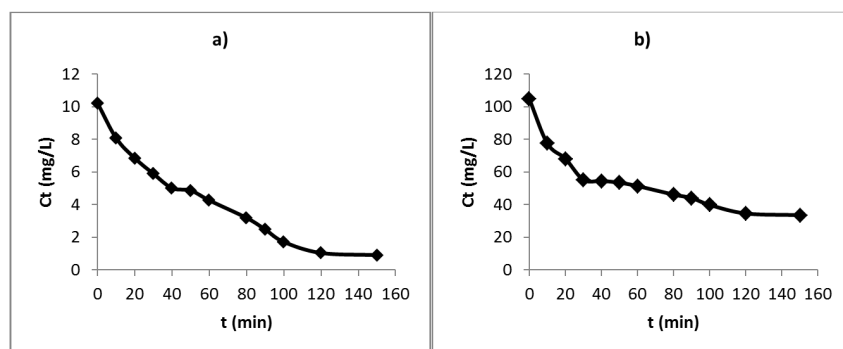


Figure 3. Evolution of the concentration of glyphosate according to the time.

To acquire the order of the glyphosate adsorption kinetic, four kinetic models were used [5]:

1) first order which can be formulated as

$$\ln C = \ln C_0 - k_1 t \quad (4)$$

2) second order which can be formulated as

$$\frac{1}{C} = \frac{1}{C_0} + k_2 t \quad (5)$$

3) pseudo-first order which can be formulated as

$$\ln(C_0 - C) = \ln C - k_1' t \quad (6)$$

4) pseudo-second order which can be formulated as

$$\frac{t}{C} = \frac{t}{C_0} - \frac{1}{k_2' C_0^2} \quad (7)$$

Where  $C_0$  and  $C$  are the initial concentration and concentration of glyphosate at any time respectively,  $t$  is time and  $k_1$ ,  $k_2$ ,  $k_1'$  and  $k_2'$  are rate constants for first order, second order, pseudo-first order and pseudo-second order models, respectively.

The applicability of the four models was checked by

plotting  $\ln C$  versus  $t$  for first order,  $1/C$  versus  $t$  for second order,  $\ln(C_0 - C)$  versus  $t$  for pseudo-first order and  $\frac{t}{C}$  versus  $t$  for pseudo-second order models. The rate constants  $k_1$ ,  $k_2$ ,  $k_1'$  and  $k_2'$  obtained from the slopes of corresponding linear plots are given in Table 2 together with correlation coefficients,  $R^2$ .

It can be seen that among the models used, the pseudo-second-order kinetic model has the best linear correlation coefficients which are close to 1 ( $> 0.98$ ). The adsorption rate constants are 0.0125 g.L<sup>-1</sup>.min<sup>-1</sup> and 0.0009 g.L<sup>-1</sup>.min<sup>-1</sup> respectively for 10 mg.L<sup>-1</sup> and 100 mg.L<sup>-1</sup>. In addition, the initial concentrations found for this model are close to the initial experimental concentrations. In view of the above we can say that the kinetic model which governs the adsorption of glyphosate on iron-textured soil in our study is that of the pseudo second order. Possible phenomena of this process, chemical sorption has played major role, sharing or exchange of electrons between glyphosate and iron-textured soil [21]. This result is in agreement with those found by other researchers. For example, Thiago *et al.* (2018) found that the adsorption of glyphosate to goethite is pseudo-second order as is the adsorption of glyphosate to montmorillonite [22-23].

Table 2. Parameters obtained from kinetic models applied to the adsorption of glyphosate on iron-textured soil.

Kinetic models	Initial concentration $C_0$		rate constants $k$		Correlation coefficient ( $R^2$ )	
	10 mg/L	100 mg/L	10 mg/L	100 mg/L	10 mg/L	100 mg/L
1 <sup>st</sup> order	10.40 mg/L	82.40 mg/L	0.0173 min <sup>-1</sup>	0.0076 min <sup>-1</sup>	0.9659	0.8868
2 <sup>nd</sup> order	16.31 mg/L	86.20 mg/L	0.0059 g.L <sup>-1</sup> min <sup>-1</sup>	0.0001 g.L <sup>-1</sup> min <sup>-1</sup>	0.8238	0.9505
Pseudo 1 <sup>st</sup> order	8.92 mg/L	95.31 mg/L	0.0289 min <sup>-1</sup>	0.0140 min <sup>-1</sup>	0.9795	0.8756
Pseudo 2 <sup>nd</sup> order	9.98 mg/L	102.04 mg/L	0.0125 g.L <sup>-1</sup> min <sup>-1</sup>	0.0009 g.L <sup>-1</sup> min <sup>-1</sup>	0.9981	0.9892

### 3.2.2. Adsorption Isotherms and Adsorption Models

The adsorption isotherm is a graphical representation of the amount adsorbed per unit mass or unit area as a function of the concentration of the solute at equilibrium. These adsorption isotherm studies were conducted at room temperature (27°C) with an equilibrium time of 90 min. The result is shown by figure 4. As displayed, the adsorbed amount of glyphosate increases with the concentrations of glyphosate at equilibrium. The obtained isotherm resembles that L-shaped (Langmuir) isotherm. It's characterized by a decreasing slope as concentration increases since vacant adsorption sites decrease as the adsorbent becomes covered. Such adsorption behavior could be explained by the high affinity of the adsorbent for the adsorptive at low concentrations, which then decreases as concentration increases [24].

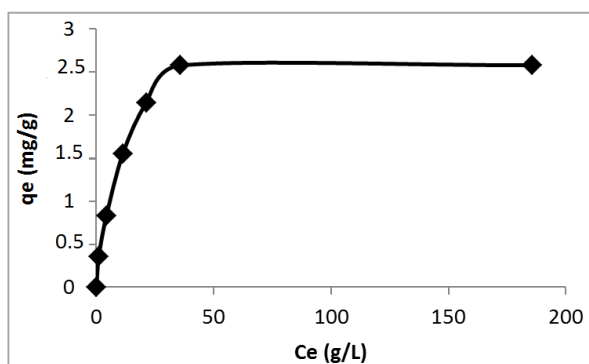


Figure 4. Isotherm of glyphosate adsorption on iron-textured soil.

In order to explain the adsorption mechanism and the quantification of the adsorbent/adsorbate affinity, two models are commonly used.

The capacity of the adsorbent for the removal of organic or inorganic substances from aqueous solutions is commonly represented by two models, Langmuir and Freundlich [3, 5]. These are the models of Langmuir and Freundlich whose equations are given by:

$$\text{Langmuir } q_e = \frac{q_m b C_e}{1 + b C_e} \quad (8)$$

$$\text{Freundlich } q_e = K_F C_e^{1/n} \quad (9)$$

where  $C_e$  (mg.L<sup>-1</sup>) and  $q_e$  (mg.g<sup>-1</sup>) are the concentration of glyphosate and the amount of glyphosate adsorbed per unit mass of adsorbent at equilibrium respectively,  $b$  (L.mg<sup>-1</sup>) is the Langmuir isotherm constants,  $q_m$  (mg.g<sup>-1</sup>) is the maximum adsorption capacity of the adsorbent,  $K_F$  is the Freundlich constant (L<sup>-1</sup>.mg), and  $1/n$  is the heterogeneity factor.

The linear forms of the Langmuir and Freundlich model are respectively:

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{b q_m} \quad (10)$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (11)$$

The application of the linear form of the Freundlich model made it possible to draw the curve

$\ln q_e = f(C_e)$  (Figure 6). The values of the parameters of this curve are grouped together in table 3. The linear correlation coefficient  $R^2$  is close to 1. In addition, the heterogeneity factor ( $n$ ) is greater than 1. Adsorption is therefore favorable. The Freundlich model can be used to describe the adsorption of glyphosate on clay, reflecting the heterogeneity of the surface of this soil [19]. This result is in agreement with the characterization of the clay which revealed several minerals and therefore a heterogeneous surface.

For the Langmuir model, we have represented  $\frac{C_e}{q_e} = f(C_e)$  in Figure 5. The Langmuir linear correlation coefficient is greater than 0.99 (Table 3). This model can therefore be used to describe the adsorption of glyphosate to this soil. There is therefore a good affinity between glyphosate and iron-textured soil. This result is in agreement with the literature. In fact, metal oxides adsorb pesticides well [24-25]. The adsorption sites of this soil are: Goethite, Fe<sub>2</sub>O<sub>3</sub> anatase (titanium dioxide) and phengite [17, 22]. The maximum amount of glyphosate adsorbed is 2.6824 mg.g<sup>-1</sup>. This soil adsorbs glyphosate well. Indeed, while Li et al., (2005) found a maximum amount of glyphosate adsorption of 184.5 mg.g<sup>-1</sup> on clay (MgAl-layer) after 24 hours of treatment, Villa et al. (1999) obtained 0.004 mg.g<sup>-1</sup> on clay (Hydrotalcites) [26-27].

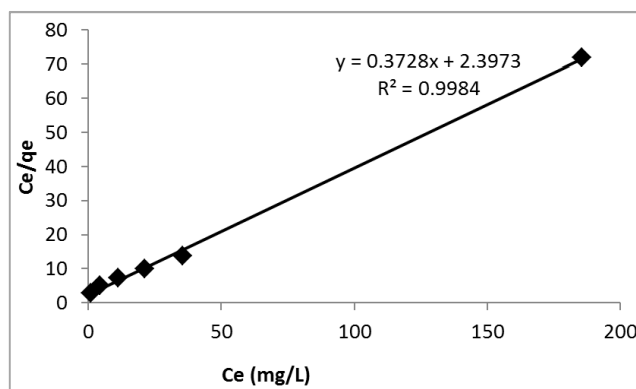


Figure 5. Application of Langmuir model to the adsorption of glyphosate on iron-textured soil.

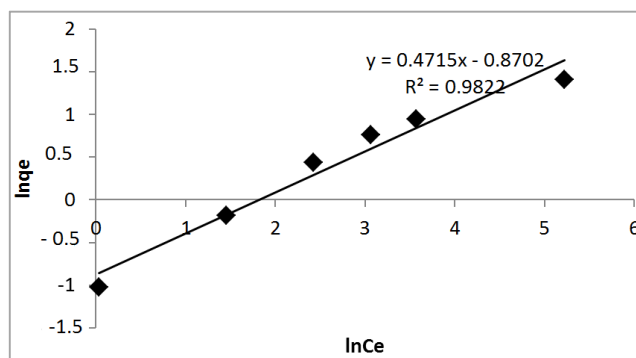


Figure 6. Application of Freundlich model to the adsorption of glyphosate on iron-textured soil.

Table 3. Parameter values of Langmuir and Freundlich models.

Model	Isotherms correlation coefficient ( $R^2$ )	$q_m$ (mg/g)	b
Langmuir	0.9984	2.6824	0.1555
Freundlich	Isotherms correlation coefficient ( $R^2$ )	$k_F$	n
	0.9583	0.4715	2.4648

### 3.3. Study of the Influence of Some Factors on the Removal of Glyphosate

#### 3.3.1. Influence of pH Solution

The pH is an important parameter in the study of the phenomenon of adsorption. The influence of pH on the adsorption of glyphosate by clay is shown in figure 7. According to the figure, the rate of elimination of glyphosate increases between pH 2 and 6 with the maximum value at pH = 5. From pH = 6, the adsorbed amount decreases to 40% at pH = 10. This is because of the acidic nature of glyphosate. The results are consistent with previous studies with glyphosate. Indeed, the impact of pH on the adsorption of glyphosate has already been demonstrated (Mcconnell and Hossner, 1985; De Jonge et al., 1999) [22] and is explained by the number of negative charges carried by the acid groups of the molecule which vary according to the pH and which modifies the electrostatic interactions with the environment [28]. Studies have shown that the phosphate group of glyphosate inter-reacts with goethite and hematite (the alpha form of  $Fe_2O_3$ ). In addition, amine and carboxylic groups could be involved. At pH Below 5.4 (pH<sub>zc</sub>), glyphosate has a negative charge at the level of the phosphate, the carboxyl group and the level of the amino group. The overall charge of glyphosate is therefore negative. There is therefore a strong interaction between the study clay and glyphosate for the pH in the 4-6 range. In addition, the phosphate group of glyphosate has a high affinity with the Ferrol ( $FeOH^+$ ) surface function of goethite in solution. The interaction between glyphosate and goethite occurs primarily with the phosphate group [18, 22]. When the medium is very acidic (pH 2-3), there are a large amount of protons ( $H^+$ ) which could lead to competition between the protons and the glyphosate thus reducing the adsorbed quantity of glyphosate [28]. At pH greater than the pH of zero charge and in particular in a very basic medium, the adsorption of glyphosate is not favored.

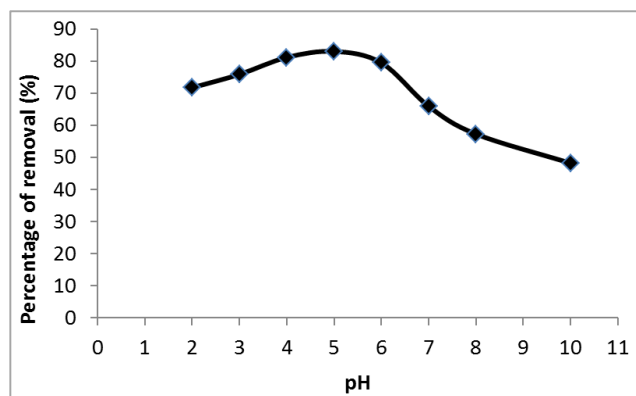


Figure 7. Influence of pH on the adsorption of glyphosate.

#### 3.3.2. Influence of Adsorbent Dose

To assess the effectiveness of the iron-textured soil in adsorbing glyphosate, the influence of variation in soil mass on the adsorption of glyphosate was investigated. Figure 8 shows the adsorbed amount of glyphosate as a function of the soil mass. We observe an increase in the elimination rate from 0 to 80% with the mass of the iron-textured soil from 1 to 4. This increase is explained by the availability of more active sites with the increase in the mass of soil. With a concentration of 25 mg/L, there would be fewer molecules to adsorb which would explain an elimination rate varying very little with the mass (between 2 and 4g).

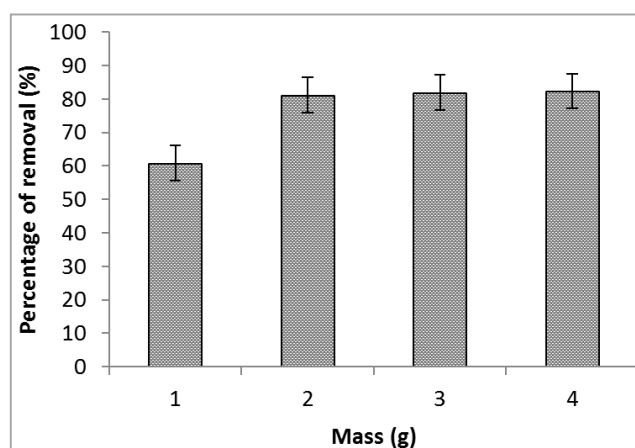


Figure 8. Influence of mass of soil on glyphosate adsorption.

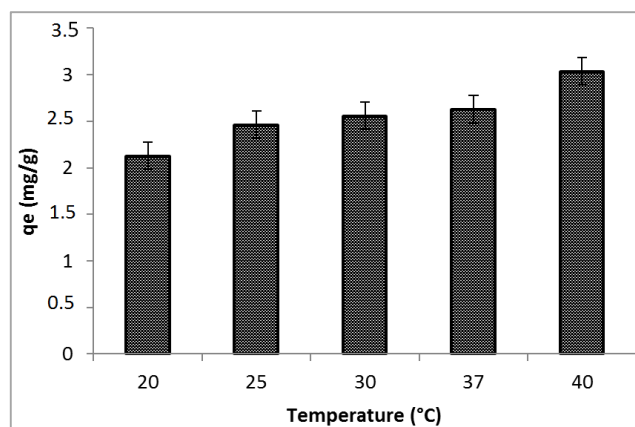


Figure 9. Influence of temperature on the adsorption of glyphosate.

#### 3.3.3. Influence of Temperature

Adsorption is a process which can be exothermic or endothermic. For this purpose, we followed the influence of temperature on the adsorption of glyphosate on clay. Figure 9 represents the variation of the adsorbed quantity of glyphosate as a function of the temperature. It is observed



that the adsorbed amount of glyphosate increases with temperature, reflecting the endothermic nature of the adsorption. The maximum amount of glyphosate adsorbed at 40°C is approximately 3 mg/g. This result is in agreement with those found by other researchers [29].

## 4. Conclusion

In this work we have studied adsorption of glyphosate on iron-textured soil. This soil is composed of various materials rich in oxide. The kinetic study of glyphosate adsorption gave an equilibrium time of 90 min. The pseudo second order model best describes the adsorption kinetics with a rate constant of 0.0009 g.L<sup>-1</sup> min<sup>-1</sup>. Also, the results have shown that the models of Langmuir and Freundlich are appropriate to describe the isotherms. The maximal amount of glyphosate adsorbed onto this soil is 2.68 mg/g. Values of these models show that the process of adsorption is physical with good affinity with adsorbent/adsorbate. It was demonstrated that the surfaces of the soils are heterogeneous. The soil of this study could well retain the glyphosate which would be available to contaminate surface water and underground water in the event of rain by leaching or infiltration.

## Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## References

- [1] Margni M., Rossier D., Crettaz P., Joliet O. (2002) Life cycle impact assessment of pesticides on human health and ecosystems. *Agriculture Ecosystems and Environment*, 93, 379-392.
- [2] Erol A., Numan H. (2005) Adsorption kinetics and isotherms of pesticides onto activated carbon-cloth. *Chemosphere*, 60, 1600-1607.
- [3] Nourouzi M. M., Chuah T. G., Thomas S. Y. (2010) Adsorption of glyphosate onto activated carbon derived from waste newspaper. *Desalination and Water Treatment*, 24, 321-326. doi: 10.5004/dwt.2010.1461
- [4] Borggaard O. K., Gimsing A. L. (2008) Fate of glyphosate in soil and the possibility of leaching to ground and surface waters: a review. *Pest Management Sciences*, 64, 441-456.
- [5] Kamalesh S., Jayanta K. D., Naba K. M. (2019) Glyphosate adsorption by Eucalyptus camaldulensis bark-mediated char and optimization through response surface modeling. *Applied Water Science*, 9 (162), 1-12.
- [6] Feng D., Soric A., Boutin O. (2020) Treatment technologies and degradation pathways of glyphosate: A critical review. *Science of the Total Environment*, 742, 1-14. <https://doi.org/10.1016/j.scitotenv.2020.140559>
- [7] Andreotti G., Koutros S., Hofmann J. N., Sandler D. P., Lubin J. H., Lynch C. F., Lerro C. C., Roos D., Parks C. G., Alavanja M. C., Silverman D. T., Freeman B. (2018) Glyphosate use and cancer incidence in the agricultural health study. *Journal of the National Cancer Institute*, 110(5), 509-516. <https://doi.org/10.1093/jnci/djx233>.
- [8] Gimsing A. L., Borggaard O. K. (2007) Phosphate and glyphosate adsorption by hematite and ferrihydrite and comparison with other variable charge minerals. *Clays Clay Mineral*, 55, 108-114.
- [9] Morillo E., Undabeytia T., Maqueda C., Ramos A. (2000) Glyphosate adsorption on soils of different characteristics. Influence of copper addition. *Chemosphere*, 40, 103-107.
- [10] Pereira R. C., Antonio C. S., Flavio F. I., Andrea P. J., Dimas A. M. Z. (2020) Interaction between glyphosate and montmorillonite in the presence of artificial seawater. *Heliyon*, 6 (3), e03532. <https://doi.org/10.1016/j.heliyon.2020.e03532>.
- [11] Day G. M., Hart B. T., McKelvie I. D., Beckett R. (1997) Influence of natural organic matter on the sorption of biocides onto goethite. II. Glyphosate. *Environment Technology*, 18, 781-794.
- [12] Castro J. V., Peralba M. C. R., Ayub M. A. Z. (2007) Biodegradation of the herbicide glyphosate by filamentous fungi in platform shaker and batch bioreactor. *Journal of Environmental Science and Health Part B*, 42, 883-886. <https://doi.org/10.1080/03601230701623290>.
- [13] Ministère de l'Agriculture de Côte D'Ivoire- ISYSPHYT.CI. (2012) Liste actualisée des pesticides homologués et autorisés en Côte d'Ivoire 31 Décembre 2012. [www.ISYSPHYT.CI](http://www.ISYSPHYT.CI)
- [14] Arlette M., Cardenas P., Jorge G. I., Ruben V. M. (2012) Determination of the Point of Zero Charge for Electrocoagulation Precipitates from an Iron Anode. *International Journal of Electrochemistry Science*, 7, 6142 – 6153.
- [15] Abo E. A., Yobouet Y. A., Kouakou Y. U., Trokourey A. (2020) Optimization of the preparation of activated carbon based on corn cobs and physico-chemical characterization. *International Journal of Innovation and Applied*, 29 (4), 1161-1171.
- [16] Wang S., Zhu Z. H. (2005) The Physical and Surface Chemical Characteristics of Activated Carbons and the Adsorption of Methylene Blue from Wastewater, *Journal of Colloid and Interface Science*, 284 (2), 440- 446.
- [17] Ilina S. M., Ollivier P., Slomberg D., Baran N., Pariat A., Devau N., Sani-Kast N., Scheringer M., Labille J. (2017) Investigations into titanium dioxide nanoparticle and pesticide interactions in aqueous environments. *Environmental Science: Nanoscience*, 00, 1-3, 1-14. Doi: 10.1039/C7EN00445A.

- [18] Dideriksen K., Stipp S. L. S. (2003) The adsorption of glyphosate and phosphate to goethite: A molecular-scale atomic force microscopy study. *Geochimica et Cosmochimica Acta.*, 67 (18), 3313–3327. doi:10.1016/S0016-7037(02)01369-8
- [19] Paszko T. (2006) Sorptive behavior and kinetics of carben-dazim in mineral soils. *Polish Journal Environmental Studies*, 15 (3), 449–456.
- [20] Jensen L. C., Fuentes R., Báez M. E., Escudey M. (2009) Adsorption of Glyphosate on Variable-Charge, Volcanic Ash-Derived Soils. *Journal of Environmental Quality*, 38, 1449–1457. doi:10.2134/jeq2008.0146
- [21] Hameed B. H., Krishni R. R., Sata S. A. (2009) A novel agricultural waste adsorbent for the removal of cationic dye from aqueous solutions. *Journal of Hazardous Material*, 162, 305–311
- [22] Orcelli T., Eduardo M., Alexandre U., Valezi D. F., Antonio C. S., Cássia T. B., Zaia D. A. M. (2018) Study of Interaction Between Glyphosate and Goethite Using Several Methodologies: an Environmental Perspective. *Water Air Soil Pollution*, 229, 150–162. <https://doi.org/10.1007/s11270-018-3806-1>
- [23] Marco-Brown J. L., Barbosa-Lema C. M., Sánchez R. M. T., Mercader R. C., Afonso M. S. (2012) Adsorption of picloram herbicide on iron oxide pillared montmorillonite. *Applied Clay Science*, 58, 25–33. doi: 10.1016/j.clay.2012.01.004
- [24] Donald L. S. (2003) Sorption Phenomena on Soils. *Environmental Soil Chemistry*; Donald, L. S., Eds.; Second Edition: Academic Press, 133–186.
- [25] Clausen L., Fabricius I. (2001) Atrazine, isoproturon, mecoprop, 2,4-D, and bentazone adsorption onto iron oxides. *Journal of Environmental Quality* 30(3), 858–869. doi: 10.2134/jeq2001.303858x.
- [26] Li F., Wang Y., Yang Q., Evans D. G., Forano C., Duan X. (2005) Study on adsorption of glyphosate (N-phosphonomethyl glycine) pesticide on MgAl-layered double hydroxides in aqueous solution. *Journal of Hazardous Material* 125, 89–95. <https://doi.org/10.1016/j.jhazmat.2005.04.037>.
- [27] Villa M. V., Sánchez-Martín M. J., Sánchez-Camazano M. (1999) Hydrotalcites and organohydrotalcites as sorbents for removing pesticides from water. *Journal of Environmental Science and Health Part B*, 34, 509–525. <https://doi.org/10.1080/03601239909373211>
- [28] Accinelli C., Koskinen W., Seebinger J. D., Vicari A., Sadowsky M. (2005) Effects of incorporated corn residues on glyphosate mineralization and sorption in soil. *Journal of Agricultural and Food Chemistry*, p 53.
- [29] Taha H. (2014) Etude de l'adsorption du COS sur des oxydes métalliques: influence des propriétés acido-basiques de surface et des compétitions d'adsorption COS-CO<sub>2</sub>-H<sub>2</sub>S. *Matériaux*. Université Pierre et Marie Curie - Paris VI, Français. fñNNT: 2014PA066243ff. Fñtel-01086574f.