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Retention of a compound of herbicides, 2,4-dichlorophenoxy acetic acid, to a soil in the absence and in the presence of Cu(II) and Zn(II) cations.

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Abstract
Soil contamination by pesticides is increasingly worrisome reality. Consequently, it is important and necessary to understand the mechanisms implied in the future of these in the soil to try to plan the risk of contamination. This work is a contribution to the identification of the main factors influencing the retention of the 2,4-Dichlorophenoxyacetic acid, as model pollutant, in two Moroccan agricultural soils. Among the main parameters influencing on the retention, we are considering the review of the influence of the complexation reactions with heavy metals susceptible that may be present in the studied soils. Therefore, we studied the retention of the 2,4-D in continuous system in presence and in absence of metal cations such as copper (II) and zinc (II). The quantity of the 2,4-D retained by the soil is analyzed by High-performance Liquid Chromatography (HPLC). The results show that the metal cations play a major role on the mechanism of adsorption of 2,4-D on the soil.

Keywords: soils, pollutants, adsorption, metal cations.

1 .Introduction

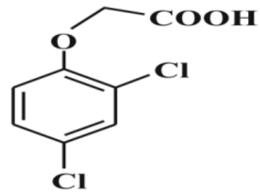
The use of pesticides in agriculture has been considered a necessary evil to ensure rapid protection of crops against insects, pests, fungi and other enemies. However, it presents a major problem in particular the diffuse pollution of many aquifers throughout the territory. Morocco imports annually from 10,000 to 12,000 tons of agricultural pesticides.

A lot of residues and metabolites of these pesticides are found in most environmental compartments water, air and soil **[1]**. The latter often behaves like a tank screws-to-screws of pesticides and metals introduced into the environment. It is a heterogeneous mixture composed of a large number constituents (organic and inorganic), the composition and surface activity are variable **[2]**.

Pesticides used are in large part of organic compounds may interact and bind to the cations of metals also present in the soil **[3,4]**. The role of these cations must not be neglected. In effect, it may induce the formation of stable complexes that modify the properties of the pesticide and any in mobility.

If the interest is focused first time on the contamination of the surface due to high concentrations detected early, the problem of soil and groundwater is topical. It is therefore necessary to study the fate of pesticides in the soil in order to better measure the environmental impact.

The main objective of this work is to study the retention of a compound herbicides well studied in our laboratory of points of view thermodynamics **[5-8]**., 2,4-D, 2,4–dichlorophenoxy acetic a Moroccan soil, as well as the influence of some metallic cations on the detention :



2,4-D

2. Material and Methods

2.1. Reagents

- Acétonitrile (H_3CCN) and acetic acid (CH_3COOH).
- Nitric acid (HNO_3), hydrochloric acid (HCl) and sodium hydroxide (NaOH).
-2,4-D : 2-(2,4-dichlorophenoxy) acetic acid
- $CuSO_4$, $5H_2O$; $Zn(NO_3)_2$, $6H_2O$.

2.2. Sampling and preparation of soil samples

The soil samples from the region of Souss (Howara) have been collected from the surface (0-20 cm) and dried in air (or in an oven at 25°C) in a room free of dust after drying. The debris on the surface are removed and reduced to a mortar. The samples were sieved to 2 mm for the analysis of all elements. They were stored at room temperature in plastic containers or in waxed cardboard boxes, free of any contamination.

2.2.1. Physicochemical characteristics of the soil

2.2.1.1. Particle size analysis of Howara soil

Particle size analysis has for aim to quantify the mineral particles grouped into basic classes, and define the size distribution of a soil. It allows classifying mineral constituent partial aggregates a number of fractions by diameter class. It is assumed that these mineral particles are spherical. The particle size analysis of the soil (table 1) shows that the fraction clay loam is the dominant.

Table 1: Particle size analysis of the soil.

Soil	% clay	% silt	% sand	texture
Howara	30	42	25	silty clay

2.2.1.2. pH and conductivity

Soil pH is related to the pH equilibrium between the solid phase of a sample of the soil and the liquid phase of the contacting solution. It is measured for a weight ratio solid / liquid 1/10. Two grams of soil are placed in contact with 20 ml of ultrapure water (table 2). The pH value of the soil shows that it is slightly alkaline soil.

Table 2: pH and conductivity of the Howara soil.

Soil	pH	conductivity ($\mu S.cm^{-1}$)
Howara	8,45	198

2.3. Pesticide use

Different physicochemical parameters of 2-(2,4-dichlorophenoxy) acetic acid, are presented in table 3.

2.4. Procedure

The adsorption tests in a batch reactor (figure 1) are made at ambient temperature 25 ± 0.1°C. A mass m (5g) of the soil is brought into contact with 25 mL of an aqueous solution of C_i adsorbate concentration (mol/L) for the desired time. The flasks were sealed and shaken (200 rpm). The mixtures were successively vacuum filtered using Whatman filter disc micro 0.45µm and subsequently analyzed by HPLC. This gives the concentration of C_r retention of solute in the aqueous phase. Access to the concentration C_{ad} adsorbed on the soil in accordance with the equation:

$$\mathbf{C_{ad} = C_i - C_r} \qquad (1)$$

The amount of pesticide retained by the soil (Q) is calculated using the following relationship:

$$\mathbf{Q\ (mol/g) = C_{ad} * V/m} \qquad (2)$$

V and m are respectively the volume of the solution in liters and the adsorbent mass in grams.

Table 3: Characteristics of 2,4-D herbicide

formula	density	molecular weight (g/mol)	pKa	temperature of Melting (°C)	Wavelength (nm)	Solubility in water (mg/L)
$C_8H_6O_3Cl_3$	1.6	221.04	2.67	138	285	900

To achieve the adsorption kinetics of a pesticide is mixed with 25 ml of ligand concentration C_i to 5 g of soil mass stirred. At given time intervals, the sample was filtered and analyzed by HPLC.
To study the effect of pH we varied the pH of the solution, the concentration of pesticide remains constant with concentrated solutions of NaOH and HCl.
The study of the effect of complexation on the retention was conducted by preparing pesticide solutions in the presence and absence of the metal.
Three trials were performed in each study to minimize the experimental error and thus ensure the reproducibility of results.

2.5. Techniques

2.5.1. Determination of the herbicide by HPLC

The determination of the concentrations of the herbicide is highly sensitive analytical methods such as high performance liquid chromatography (HPLC). The protocol was adopted by Belmouden (9)
The study of 2,4 -D was determined by HPLC with a device of HPLC Varian 9012 equipped with an isocratic pump LG, a column Hypersil C18 (length of 25 cm and a diameter of 5 mm) and UV-Visible detector PDA. The analysis is carried out in reverse phase with a mobile phase consisting of a mixture of: 49% acetonitrile, 49% water and acetic acid to 2 %. The flow rate is 0.4 mL/min. The injection volume is 20 µL.

3. Results and discussion

A systematic study of the retention of 2,4-D on the Howara soil (HW) was conducted. It examines the various parameters that influence retention: the effect of relative soil mass / volume of solution, the kinetics of retention, the effect of pH of the medium and finally the effect of complexation of 2,4 -D with the Cu(II) and Zn(II).

3.1. Effect of relative soil mass / volume of solution

This study is to determine the ratio of soil mass / volume of solution leading to minimum removal rate maximum of the compound 2,4-D. It is performed for an initial concentration of 2.10^{-3}M by varying the mass of 1.25 g to 10 g of the soil while keeping the volume of the solution to 25 mL. The contact time is 24 hours.

Figure 1 shows the positive effect of soil by report mass / volume of solution on the retention capacity of 2,4-D by the soil HW.

In addition, the increase in the mass of the adsorbent causes the efficiency of retention of the herbicide. This improvement is due to the surface area that is larger at higher values of the ratio (m(soil)/v(solution)). A small quantity of adsorbent is saturated more quickly than quantity reported. 200 mg / l (5 g of soil) seems sufficient to achieve the result of our research in a manner analogous to the results reported by Belmouden (9).

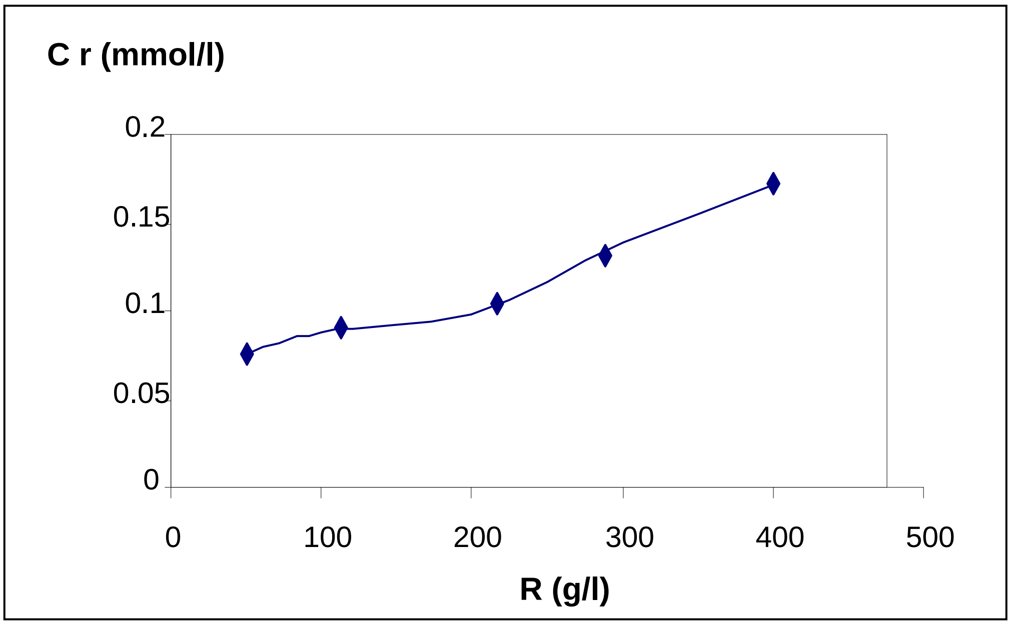


Figure 1: Variation of the concentration selected from 2,4-D according to the ratio : m (soil)/ v (solution) to 25°C, t = 24 h, $C_i = 2.10^{-3}$M

Finally, the report soil mass/volume of the solution shows a negative effect on the adsorbed amount of 2,4-D as follows (figure 2) :

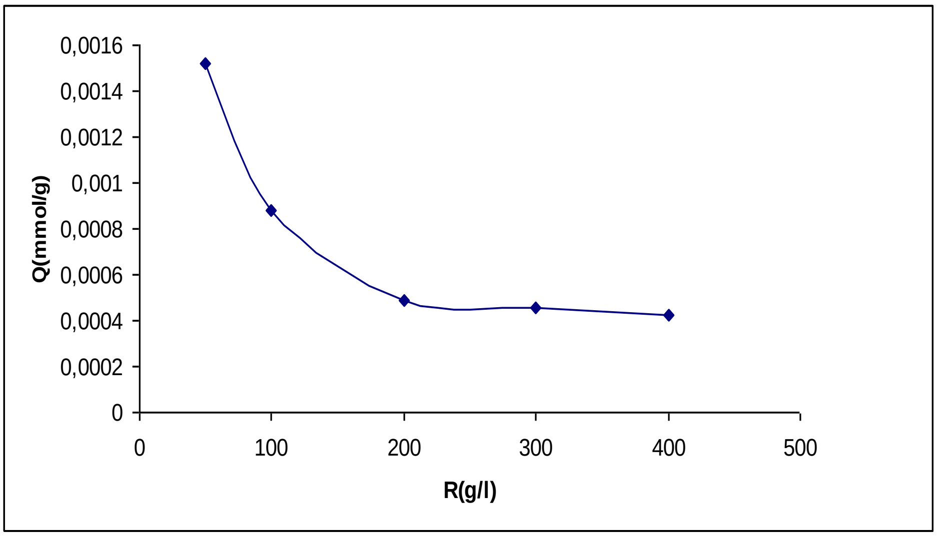


Figure 2: Variation in the amount of 2,4-D retainer according to the ratio : m(soil)/v(solution) to 25°C, t = 24 h, $C_i = 2.\ 10^{-3}$M

The Figure 2 shows that the quantities used are maximum values for the low ratios, then they are declining and then stabilize for a report of R = 200 g/L corresponding to 5 g of soil. This variation is due to an increase in the area of soil for low grain ratios and thus the availability of a large number of free sites support molecules.
The decrease in the quantity selected may be attributed to the desorption of the fraction of labile compound adsorbed due to the increase of collisions inter-particles when the mass increases.

3.2. Retention kinetics of 2,4-D by Howara soil

This study was conducted by varying the contact time from 30 minutes to 24 hours and maintaining the concentration of 2,4-D 2. 10^{-3} M, the temperature at 25°C and relative m(soil)/v(solution) to 200 g/L, the pH of the solution being 3.27.

From figure 3, the adsorption of 2,4-D from the soil (HW) is done in two steps :
- In the first step, the adsorbed amount of 2,4-D from the soil (HW) increases with contact time.
- In the second step, a plateau is reached where the solute is maximum adsorption.

The time required to reach equilibrium is 5 h 30 min. This time is consistent with the kinetic data Belmoden (9). Cheals et al. (10) gives an equilibrium time of 5 hours to the study of the adsorption of 2.4 -D on clay and sandy soils. The study by Touyer (11) on the conservation of 2,4 -D shows an equilibrium time of 7 hours.
On after the value of the amount retained by the soil, which is low and does not exceed 6%. Can explain this result the intensity of the link that may exist between the soil pH is the acidity of the pesticide. Pussemier et al. (12) reported that the adsorption of 2,4-D varies depending on the pH of the soil, and it becomes lower when working in a soil pH of above the pKa of the pesticide.

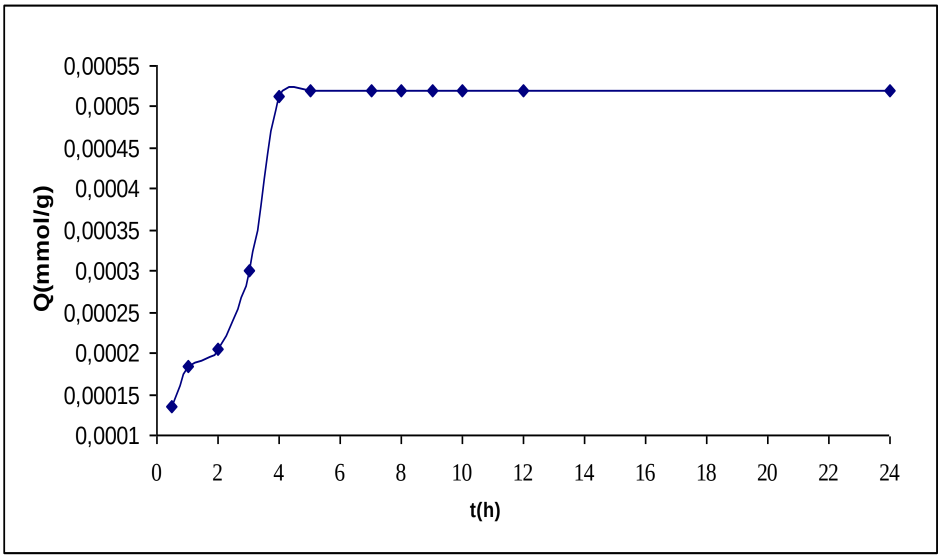


Figure 3: Adsorption kinetics of 2,4-D on the HW soil.
(t = 8 h, C_i = 2. 10^{-3} M, T = 25°, m(soil)/v(solution) = 200 g/L, pH = 3.27)

3.3. Effect of pH

For three pH values: 2, 4, and 6, we have studied the adsorption of [2.4 -D] to 2 mmol/L, a report m(ground)/v(solution) = 200 g/L, the contact time of 6 hours and a temperature of 25°C (figure 4). These results show a higher adsorption for the pH very acid. This shows that it is the molecular form ligand 2.4 -D, having a pKa of 2.67 (6-8), is the most favourable for the adsorption on the soil. Molecular Form of 2,4 -D can in fact be absorbed by hydrogen bonds through the COOH group (13). The carboxyls function of pesticide which is able to interact with the hydrogen bonds with polar groups carboxyl, hydroxyl and the components of soil oxygen.

3.4. Effect of 2,4-D complexation with Cu(II)

Many studies have been published on the sorption of pesticides and metals on ternary pesticides / metals / soil (or soil components). There are few studies on glyphosate (14) and chlordimeform (15,16). They studied initially in the solution of glyphosate complexation with copper (4) and the pesticide sorption on goethite (17), and finally, they studied the ternary system glyphosate / copper / goethite (18). Their results indicate a strong influence of the metal on the sorption of glyphosate.
Also, studies have shown that the presence of Cu (II) enhances the adsorption of glyphosate on soils and goethite (19,20) and decreases on montmorillonite (21). FLOGEAC (22) showed that the complexation of amitrole by heavy metals such as copper, iron and manganese favours its adsorption onto the ligno-cellulosic residue (fraction of soil organic matter), as well as on the soil.

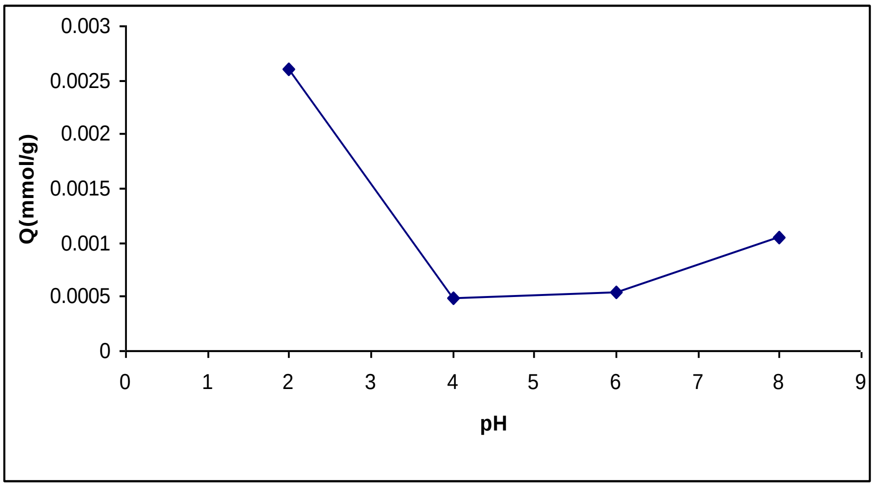


Figure 4: Variation in the amount of 2,4-D retained on the HW soil in function of pH.
(t= 8 h, C_i = 2. 10^{-3} M, T = 25°, m(soil)/v(solution) = 200 g/L, pH = 3.27)

It would be interesting to study the effect of the presence of cupric ions on the retention of 2,4-D which shows interactions complexation with Cu(II) at relatively low pH (6). For this study, two pH values are considered: pH 4 and pH 7. Various reports ligand / metal are studied: 2.5, 5 and 10. The concentration of the ligand is attached to 2 mmol/L, we vary the concentration of the metal. The same operating conditions are maintained: R (m(soil)/v(solution)) = 200 g/L ; time = 6 hours and temperature is 25°C.

a) Study at pH = 4:

The data in figure 5 clearly show a positive effect of the complexation of copper (II) on the adsorption of the 2.4-D. This effect is confirmed by the increase of the adsorption, which is inversely proportional to the ratio (ligand/metal) that is to say, proportional to the quantity of the metal.

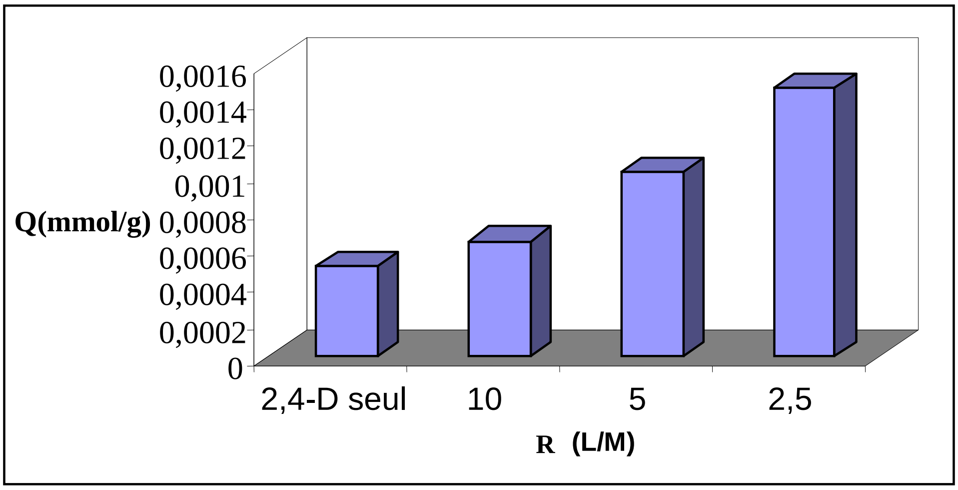


Figure 5: Retained amount of 2,4-D on the HW soil in the presence of Cu(II) at pH = 4.

In addition to the effect of the complexation, when the metal cation is present in the soil solution, it may be adsorbed on the surface thereby releasing H^+ ions by cation exchange and promoting the molecular form of the 2,4-D which adsorbs better than the ionic form.

b) Study at pH = 7:

The results presented in figure 6 show the opposite effect to that observed for pH = 4. Indeed, there is a decrease in the presence of metal adsorption at pH = 7. This can be explained by the formation of hydroxylated species Cu(II) form more insoluble the amount of metal is high ratio (Ligand /Metal).

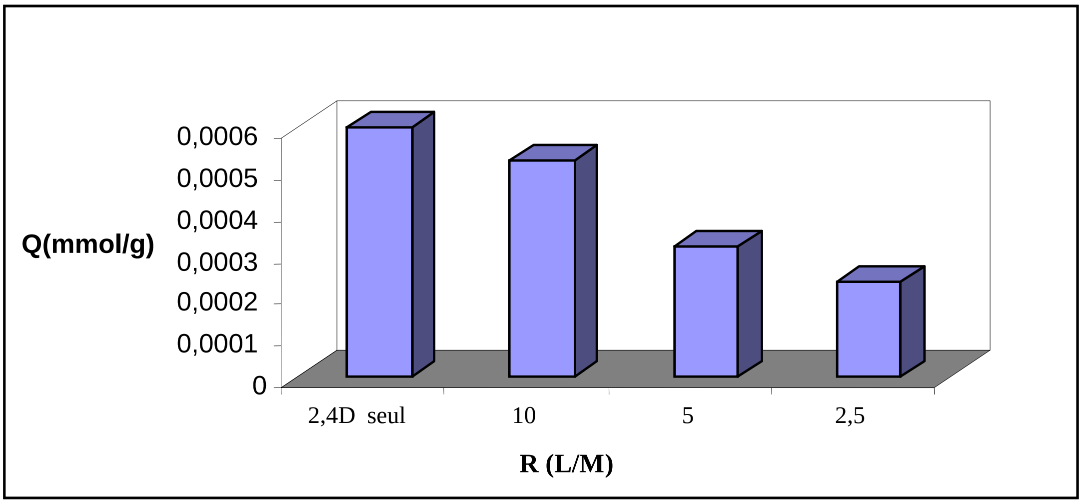


Figure 6: Retained amount of 2,4-D on the HW soil in presence of Cu (II) at pH = 7.

3.5. Effect of the complexation of 2,4-D with the Zn(II)

To study the effect of Zn(II) on the adsorption of 2,4-D on the soil, the same operating conditions are shown (figures 7 and 8). For a ratio (Ligand/Metal) = 5, we find the favourable effect of the complexation of zinc(II) on the adsorption of 2,4-D.

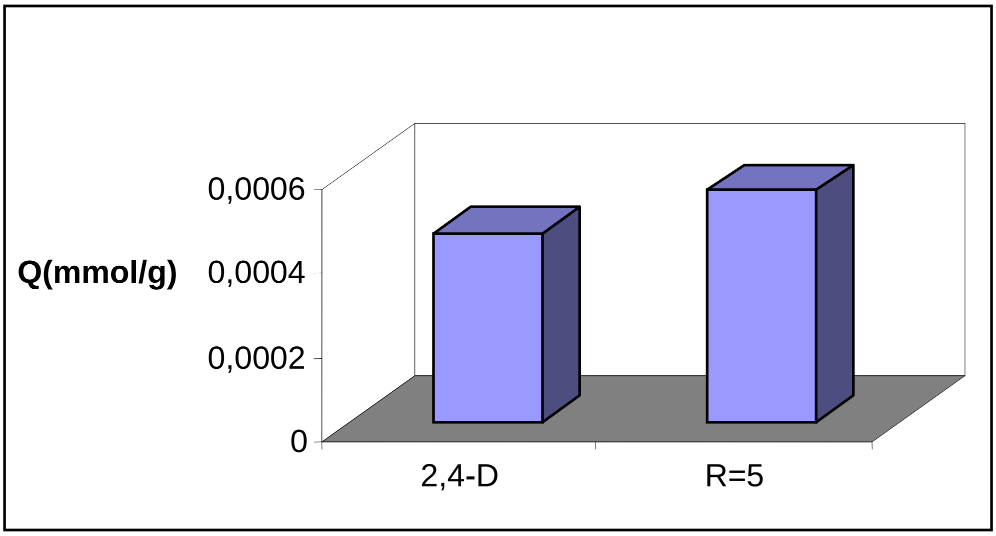


Figure 7: Retained amount of 2,4-D on the HW soil in the presence of Zn (II) at pH = 4.

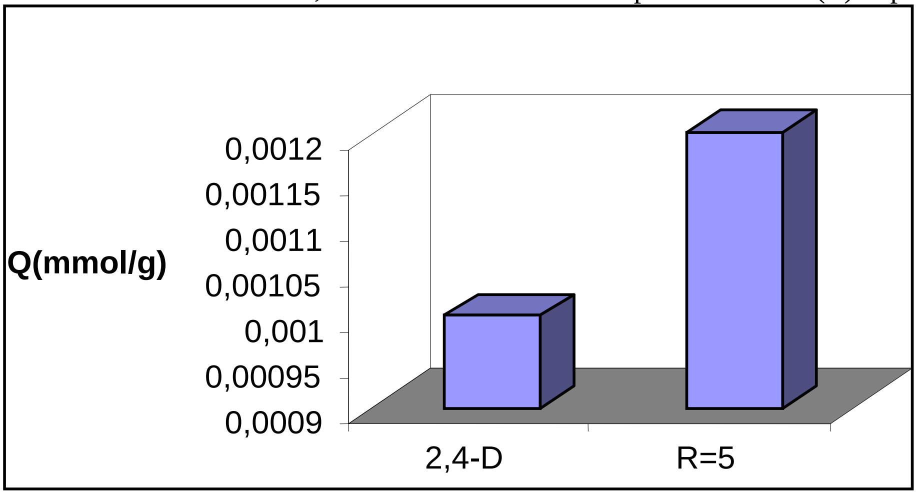


Figure 8: Retained amount of 2,4-D on the HW soil in the presence of Zn (II) at pH = 8.

Conclusion

Tracking the fate of herbicides used in agriculture such as 2,4-D in soil in the absence and presence of heavy metals, is one of the important issues discussed in the field of agriculture. Indeed, the metals can have an influence on the adsorption of the pollutant by complexing effect.
From after the results in this work, we can conclude that:
- The comparative study of the adsorption of 2,4-D in the absence and the presence of Cu^{2+} and Zn^{2+} on the soil Souss region (Morocco) showed significant differences in the behavior of soils towards the compound of the herbicide, 2.4-D alone or as if by the complexed metal ions.
- Indeed, for the adsorption of 2,4-D alone, the study of the influence of pH shows that the molecular form of 2,4-D is the most favourable adsorption.
- Finally, the presence of metal cations (Cu^{2+} and Zn^{2+}) in the soil is likely increases the rate of binding of 2,4-D on the Howara soil.

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