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Adsorption and mobility of veterinary compounds on Moroccan soil; Case of Ivermectin

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Abstract: Ivermectin (IVR) is an antihelmitic and anti-parasitic substance used mainly in veterinary medicine worldwide. Its release in the environment could have a negative effect on living organisms and generate soil and groundwater pollution. The main objective of this work aimed at the study of the adsorption of IVR on soil from Gharb region in Morocco. Sorption tests were carried out according to conventional guideline by varying the mass of the adsorbate and the pH of the solution. Analysis was made by UV-visible spectrophotometer. Adsorption kinetics of IVR was rapid and equilibrium was reached within 20 minutes. The Freundlich and Langmuir isotherms models were compared and adsorption constants were calculated. Comparison between the two models showed that Freundlich model fitted best data while kinetic data fitted pseudo-second order. Thermodynamically, sorption process of IVR on the examined soils would be exothermic and controlled by physisorption Tests of mobility have shown strong adsorption of IVR in the soils tested After 7 batches of water percolated, less than 2% of the applied quantity has been detected.

Keywords: *Ivermectin; Soils; Adsorption; Mobility*

1. Introduction

The intensive use of veterinary pharmaceuticals, particularly antibiotics and pesticides in the production of domestic animals, has resulted in a significant release of chemicals into the environment. The environmental risk of veterinary drugs has given rise to much earlier concern than drugs for human use (Blume *et al.*, 1976). They reach the soil directly as they are applied in intensive farm production. Avermectins are an important group of veterinary drugs including (Abamectin, Avermectin Doramectin, Moxidectin). Their widespread use could have an environmental risk (Campbell *et al.*, 1983, Strong *et al.,* 1987, Shoop *et al.,* 2002). Ivermectin (IVR) is reported to be very immobile and should not be readily transferred to groundwater while it remains subject to be transported surface water polluted by with animal wastes (Bloom *et al.*, 1993). The Molecule of IVR is sensitive to

ultraviolet radiation that causes isomerization of double bonds (Hennessy et Alvinery, 2002), with environmental consequences related to its degradation. It has also been shown to undergo rapid photodegradation when deposed as a thin dry film on glass, with an estimated half-life of approximately three hours (03h) under the summer sun (Bloom *et al.*, 1993, Halley *et al.,* 1989b, Liebig *et al.,* 2010). Water solubility provides an indication of the maximum IVR concentration that varies between 4 and 5 ml/Lin the aquatic environment (Bloom *et al.*, 1993, Lo *et al.,* 1985).The adsorption coefficient, expressed on the basis of soil organic carbon (K_{oc}) for IVR would be between 12600 and 15700 (Bloom *et al.*, 1993, Halley *et al.,* 1989a, Krogh *et al.,* 2008). These values indicate a very strong bounding to the soil (table1). Several studies have focused on the exposure and effects of IVR on the environment (Edwards *et al.*, 2001, Boxall *et al.,* 2004, Floate *et al.,* 2005, Kolar *et al.,* 2006). These studies were designed to determine whether the use of this drug would cause harmful or undesirable effects on the environment (Halley *et al.*, 1989a). The composite prepared from hydroxyapatite was used successfully for toxic heavy metals removal (Errich *et al.*, 2021, El Hammari *et al.*, 2022).
In Morocco, no study has yet been carried out on the release of this product in the environment. This has incited us for investigating the effects of the use of IVR on the soil and water in the region of Gharb, known for its high potential of breeding activity and an intensive use of IVR (Figure 1).

Table1. Ivermectin physicochemical properties (Bloom *et al.*, 1993, Halley *et al.*, 1989b, Liebig *et al.,* 2010, Lo *et al.,* 1985, Halley *et al.,* 1989a, Krogh et al., 2008)

Molar mass (g/mol)	875
Melting point (°C)	349.8 (east)
Melting temperature (°C)	155
Gross chemical formula	$C_{95}H_{146}O_{28}$ $C_{48}H_{74}O_{14}$ (22,23-dihydroavermectin B=1a) $C_{47}H_{72}O_{14}$ (22,23-dihydroavermectin B=1b)
Vapor pressure (mmHg)	1.5×10^{-9}
Octanol/ water coefficient (K_{ow})	1651
Solubility (mg/L)	4-5
Distribution adsorption coefficient (K_{oc}) ($cm^3.g^{-1}$)	12600-15700
UV adsorption	Maxima 237, 245 et 253 nm
$T_{1/2}$ under the summer sun	3h
$T_{1/2}$ in water	12h-39h
$T_{1/2}$ in soil	1 to 2 weeks
pKa	Neutral at all pH values
LD_{50}(mg/kg)	10

2. Methodology

2.1 Presentation of Gharb region

Gharb region is located in the northwest of Morocco (figure 2) and currently covers an area of 7990 km^2 representing 1.12% of the national area. It is an important irrigated agricultural area of Morocco, characterized by a humid temperate Mediterranean climate with an Atlantic influence favorable to the development of a range of crops, fertile land dominated by sandy and clayey soils, as well as abundant water resources (ORMVAG, 2000, Omrania *et al.*, 2019, Aziane *et al.,* 2020, Lahmar *et al.,* 2019; Marouane *et al.,* 2014,).

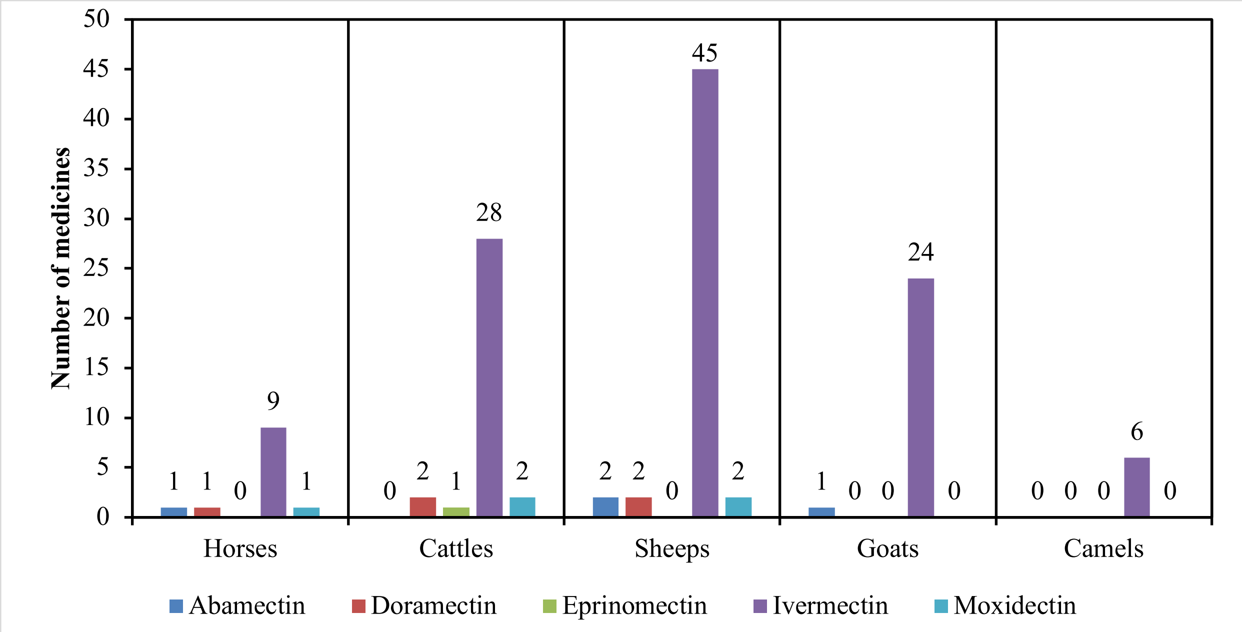


Figure 1. Statisctics of use of Ivermectin and other Avermectins in Morocco (http://www.onssa.gov.ma/fr/)

The region has an immense and rich central plain with rich and varied soils that can be grouped into four groups with varied agronomic vocation: 15% hydromorphic soils for rice growing and fodder crops; 40% black soils for cereals and market gardening; 30% black clay soils favorable to industrial crops such as sugar cane, beets and sunflowers; 15% red soils which are very rich (ORMVAG, 2000). Breeding takes an important place among the activities in the region, with a large and diverse herd estimated at 1,528,750 head constituted by 73% sheep, 24.5% cattle and 2.4% goats. The region is characterized by a bovine herd of 222,720 head, characterized by the introduction of significant genetic potential (Holstein and Black pie) and modern management (food, health, hygiene) Cattle of the improved type (Srairi *et al.*, 2003).

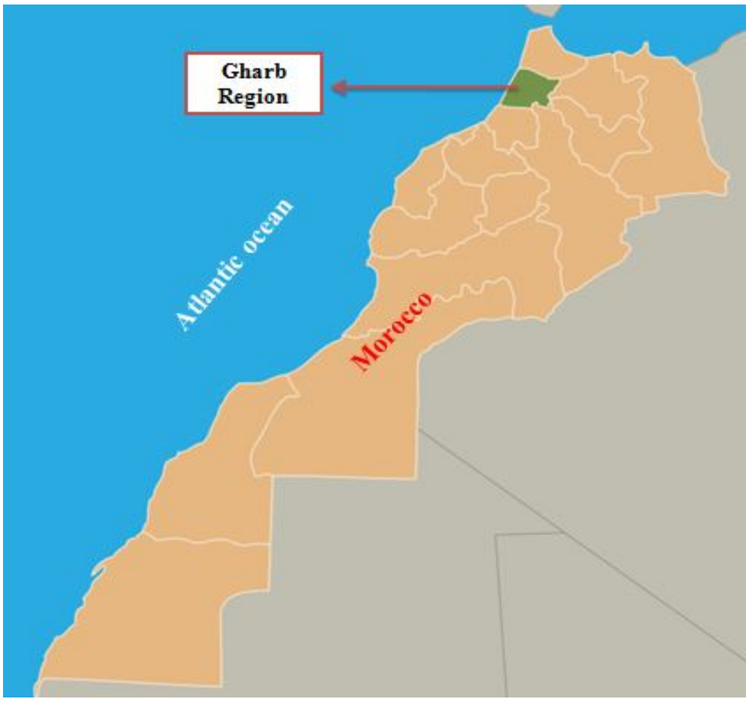


Figure 2. Location of the Gharb region

2.2 Soil sampling

Different soils (Msol and Nsol (from Mograne location) and Psol (from Sidi Allal Tazi location)) were collected at 0-25 cm depth. The samples were air-dried, sieved to a particle size < 2mm, and stored in glass vials at room temperature until used (Figure 3). The textural composition and are provided in Table 2.

Table 2. Physicochemical properties of soils

Samples	%Clay	%Silt	%Sand	%CaCO3	humidity	pH(water)	pH(KCl 1 N)	OM (%)	P_2O_5 (ppm)	K_2O (ppm)
Msol	34.4	60.7	4.9	35.2	4.8	7.2	6.6	3.4	34.6	358.5
Nsol	45.1	52.6	2.3	11.8	4.1	7.8	6.7	3.6	26.7	457.9
Psol	48.8	41.2	10.1	13.6	2.3	7.3	6.7	3.8	53.2	964.0

*Psol= SidiAllal Tazi; Msol&Nsol= Mograne

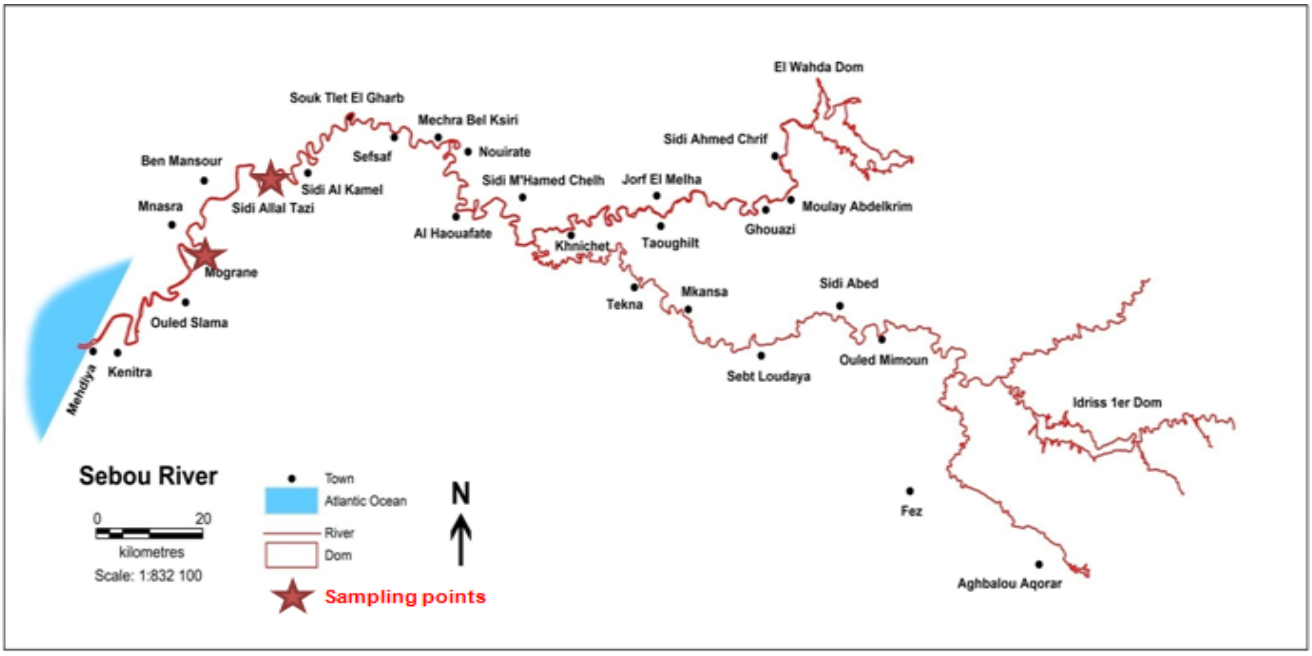


Figure 3. Sampling points in Gharb region

2.3 Standard of Ivermectin

IVR (22, 23-dihydroavermectin B_{1a} + 22, 23-dihydroavermectin B_{1b}) was purchased from Sigma-Aldrich (Germany) with 99% purity. In its pure state, IVR is a white to yellowish crystalline powder with a crude chemical formula of $C_{95}H_{146}O_{28}$, IVR is nevertheless insoluble in water; its solubility is of the order of 4 mg/L or less (Figure. 4).

2.4 *Spectrophotometer analysis*

The absorbance was measured using a UV-visible spectrophotometer type Jenway 670 5B0 at the wavelength relative to the maximum of absorption (248 nm) that corresponds to the maximum band of the spectrum of IVR (figure 5).

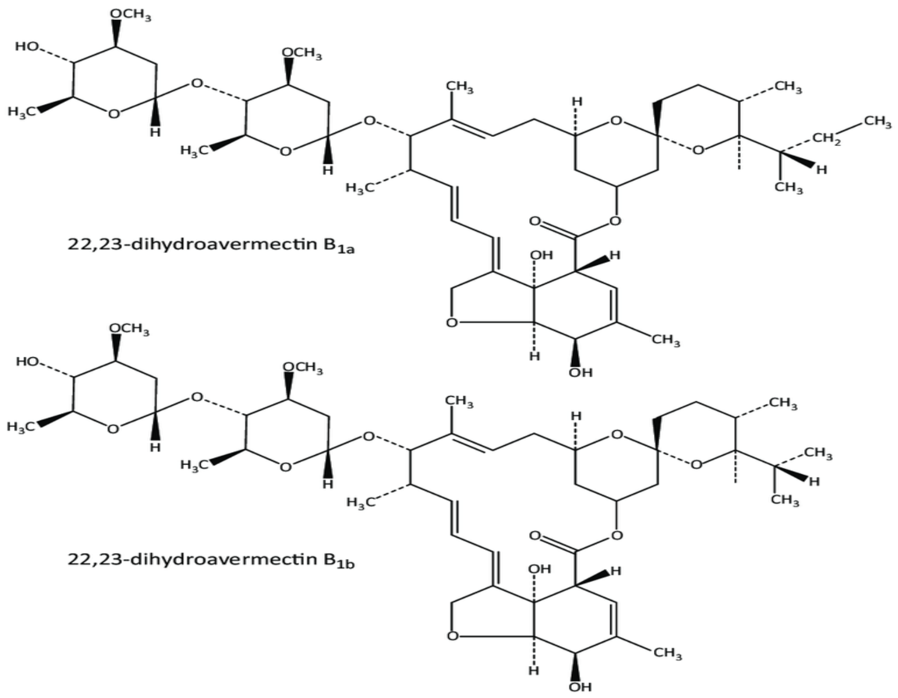
2.5 Stock solution and calibration curve of IVR

A stock solution of IVR at the concentration of 1.0 mg/mL (1000 ppm) was prepared in methanol. For recovery experiments, various standard solutions of IVR in methanol were prepared. The stock solution and all standard solutions were stored at -18°C. Ivermectin UV absorption at different concentration

has given the calibration curve presented in (Figure 6). A good linearity was obtained in the range of concentration used, with a regression coefficient of 0.999. This analytical technique was retained for the subsequent experiments.

2.6 Kinetics of adsorption

Preliminary test of dissipation of IVR in aqueous solution showed degradation within 3 hours. Kinetics of adsorption of IVR was tested with 50mg the soil in a 20 mg/L of IVR. Tests showed rapid achievement of the equilibrium within less than 5hours. To avoid degradation in the solution, duration of 1 hour was retained for the subsequent test of adsorption. Data was tested to fit pseudo first or second order model.



IUPAC name - 22,23-dihydroavermectin B_{1a} + 22,23-dihydroavermectin B_{1b}
Formula - C48H74O14 (22,23-dihydroavermectin B_{1a}) + C47H72O14 (22,23-dihydroavermectin B_{1b})

Trends in Parasitology

Figure 4. Chemical structure of Ivermectin

All the other reagents chemical and solvents (methanol, acetone) were analytical grade;

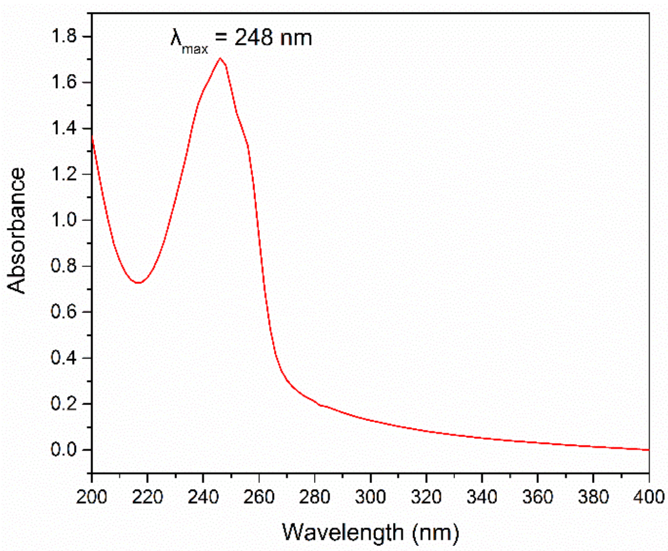


Figure 5. UV spectrum of Ivermectin variation

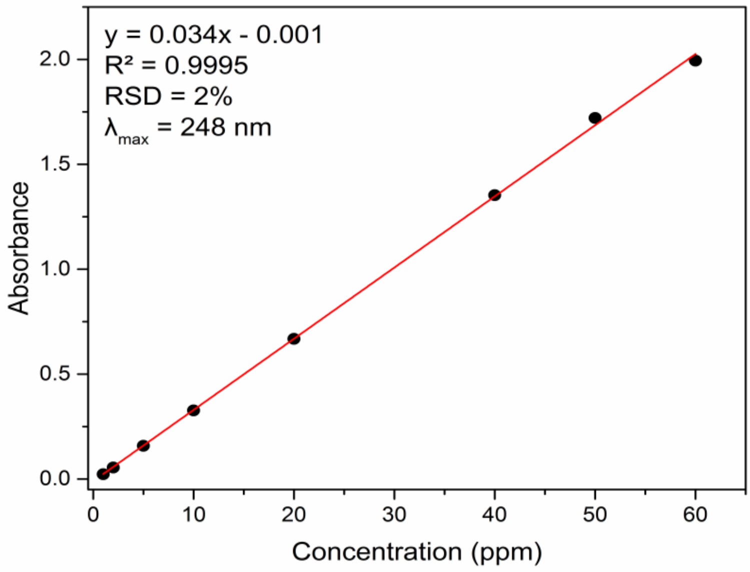


Figure 6. The calibration curve of Ivermectin

Adsorption tests

Adsorption of IVR by soil was performed in batch experiment. A quantity of soil tested (50 mg) was introduced into 50 mL of IVR aqueous solutions at 20 mg / L. The mixture was subjected to agitation at room temperature for 1 h to reach equilibrium at constant pH (6.5), then centrifuged at a speed of 3000 rpm for 30 minutes and filtered to separate the solid and water phases. The solution was analyzed for the remaining residue. The sorption efficiency was evaluated by the determination of the sorption capacity of adsorbent noted q_a or the retention rate %R of the adsorbate according to the following equations Eq. (1) (Kali *et al.*, 2022), Eq. (2). Tests were performed in duplicate and the mean values are considered.

$$Qa = (C_0 - C_e).\ V/m \quad \textbf{(Eq.1)}$$

$$R\% = (C_0 - C_e / C_e)\ .100 \quad \textbf{(Eq.2)}$$

C_0 and C_e are the initial concentration and the equilibrium concentration of the adsorbate (mg/L), respectively, V (L) is the volume of the suspension and m (g) the mass of the adsorbent.

Data of adsorption were tested to fit adsorption models of Langmuir Eq (3) and Freundlich Eq (4). The best fitting model was used to draw the main adsorption parameters.

$$\frac{1}{Q_e} = \frac{1}{bQ_m}\frac{1}{C_e} + \frac{1}{Q_m} \quad \textbf{(Eq.3)}$$

$$Ln(Q_e) = \frac{1}{n}Ln(C_e) + Ln(K) \quad \textbf{(Eq.4)}$$

2.7 Effect of mass and pH on the adsorption of IVR

Effect of the mass of adsorbent

Variation of the mass of adsorbent could have an influence on the quantity of IVR adsorbed. The effect of the mass was evaluated using five values of the mass of the soil (20, 50, 100, 150 and 200 mg) in 50 mL solution of 20 ppm of the IVR. The mixture was subjected to agitation at room temperature for 1h at constant pH, samples were centrifuged and filtered and the absorbance was measured using a UV-visible spectrophotometer.

Effect of pH

During an adsorption study, the pH of the solution is an important parameter which must be taken into consideration. Five (5) types of solution of 20 mg/L in IVR (50 mL) at different pH (2, 4, 6, 8 and 10) and 50 mg of soils, tests were conducted as described before for the effect of the mass.

2.8 ***Study of the mobility of Ivermectin in soils***

The mobility study was carried out using soil columns, three types of soils studied (Psol, Msol and Nsol) previously sieved and air-dried (table 2). Six PVC (2 for each soil) tubes with a height of 37 cm, consisting of 7 rings (5 cm high and 10 cm in internal diameter) closed at the bottom by muslin material to retain the soil . Columns were packed with the soil and left for saturation by suction overnight. Ivermectin (99% purity), distilled water was used for percolating the columns according to leaching guideline (OECD 312, 2004). An amount of Ivermectin (5 mL) from stock solution (1000 ppm) was applied on the top of each column at 1 cm of the surface (OECD *312*, 2004). Soil percolation was conducted using a peristaltic pump. Flow rates were maintained at 2 ml/min. The eluted solution was collected in 100 ml fractions. The concentration of IVR was determined using a UV spectrophotometer at a wavelength of 248 nm (Figure 7).

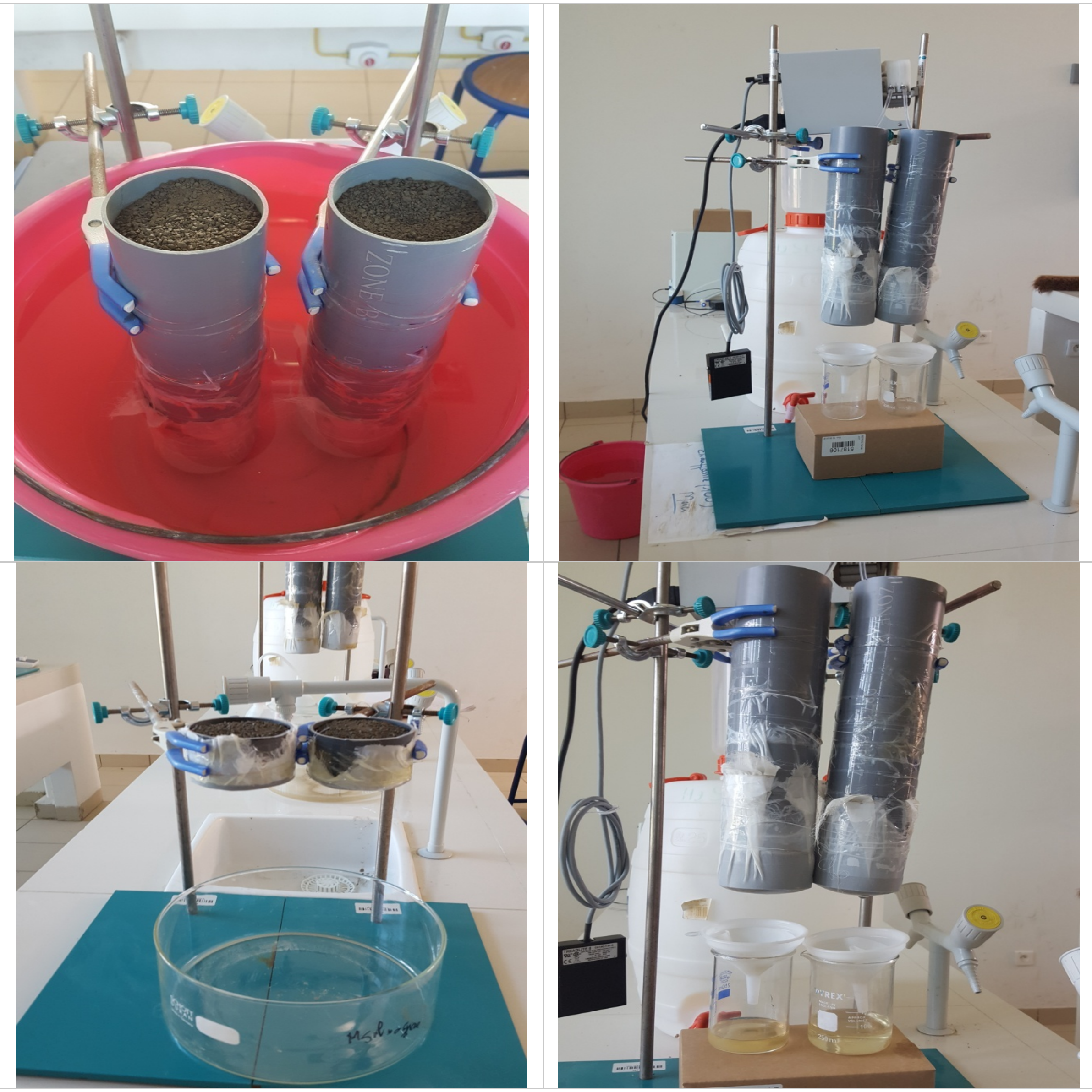


Figure 7. Mobility of Ivermectin in the soils from Gharb region Psol, Msol and Nsol

The rest of the mobility test was carried out with 5 cm high rings filled with soil and percolated with distilled water. The percolated solutions were collected in 50 mL fractions and analyzed for their IVR content.

3. Results and Discussion

3.1 Adsorption kinetics

Figure 8 shows the kinetic of adsorption curves of IVR in the soils studied. The kinetics is rapid and the maximum is rapidly quickly achieved for all soils studied .This reflects the high adsorptive affinity of IVR to the soil as it was reported by various authors (Savci, 2015). The maximum adsorption is achieved in few minutes for all soils.

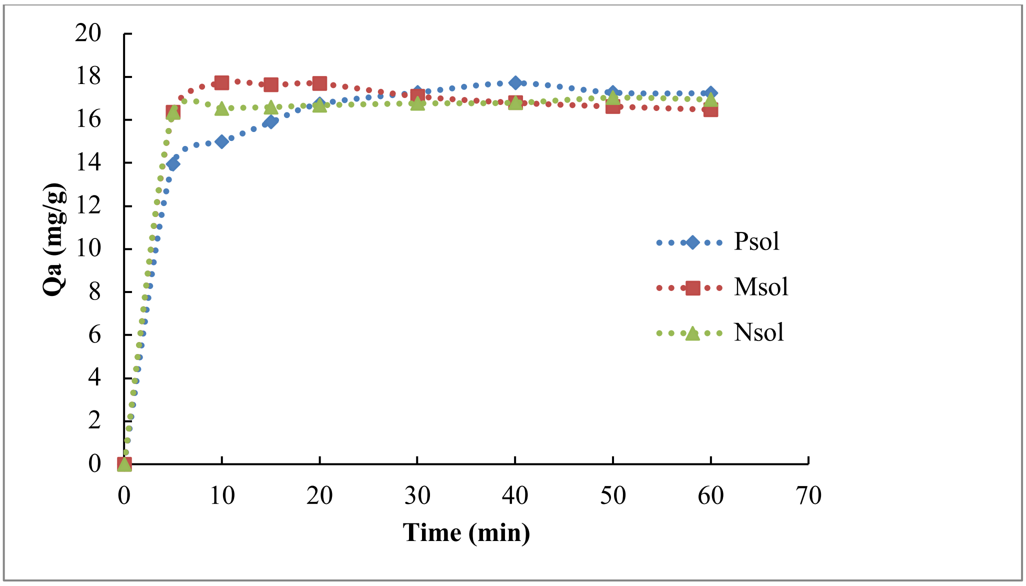


Figure 8. Adsorption kinetics of the Ivermectin in soils studied

To elucidate the kinetic parameters of adsorption in the different soils, two mathematical models were tested for their fitting to data, namely first and second order. The two models are represented by their logarithmic equations 5 and 6 (Bouzidi *et al.*, 2021); Data related to the first and second order are presented in table 3.

$$\log(qe\text{-}qt) = \log qe - \frac{K1}{2.303} t \qquad \text{(Eq.5)}$$

$$\frac{t}{qt} = \frac{1}{K2.qe^2} + \frac{1}{qe} t \qquad \text{(Eq.6)}$$

With:

qt and qe: Quantities of adsorbate per unit mass of adsorbent respectively at time t and at equilibrium (mg / g), t: contact time (min),

K1 and K2: speed constants respectively for the pseudo-first order (min^{-1}), pseudo-second order ($g.\ mg^{-1}.\ min^{-1}$) kinetic equation.

Data presented in the table 3 show that pseudo-second order model fit very well data for all the soils. Values of regression coefficient are being very high for pseudo-second-order than first-order model. In addition, Figure 9 shows the good linearity of logarithmic plots of pseudo-second order model for the three soils.

Table 3. Kinetic model parameters

Samples	Pseudo-first order $\log(qe-qt)=\log qe-\frac{K1}{2.303}t$ (Eq.3)			Pseudo-second order $\frac{t}{qt}=\frac{1}{K2qe^2}+\frac{1}{qe}t$ (Eq.4)		
	Qe cal (mg/g)	K_1 (min-1)	R^2	Qe cal (mg/g)	K_2 (g/mg/min)	R^2
Psol/IVR	16.73	0.52	0.395	16.73	0.056	0.998
Msol/IVR	17.67	0.27	0.387	17.67	0.036	0.999
Nsol/IVR	16.67	0.33	0.103	16.67	0.015	0.999

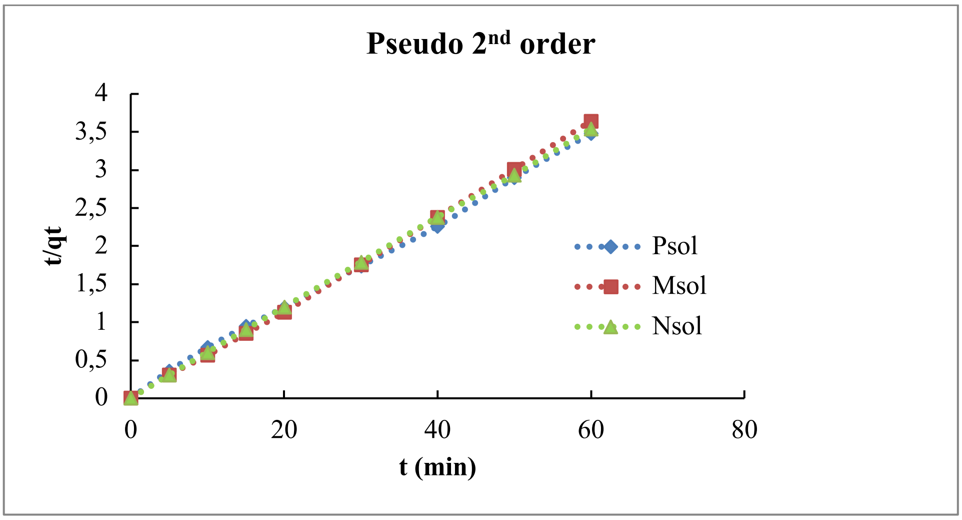


Figure 9. Plots of pseudo-second-order kinetics of Ivermectin adsorption on soils (Psol, Msol and Nsol)

3.2 Adsorption isotherms

Figure 10 shows the variation of the quantity adsorbed as a function of the equilibrium concentration of IVR on the studied soils (Psol, Msol and Nsol).

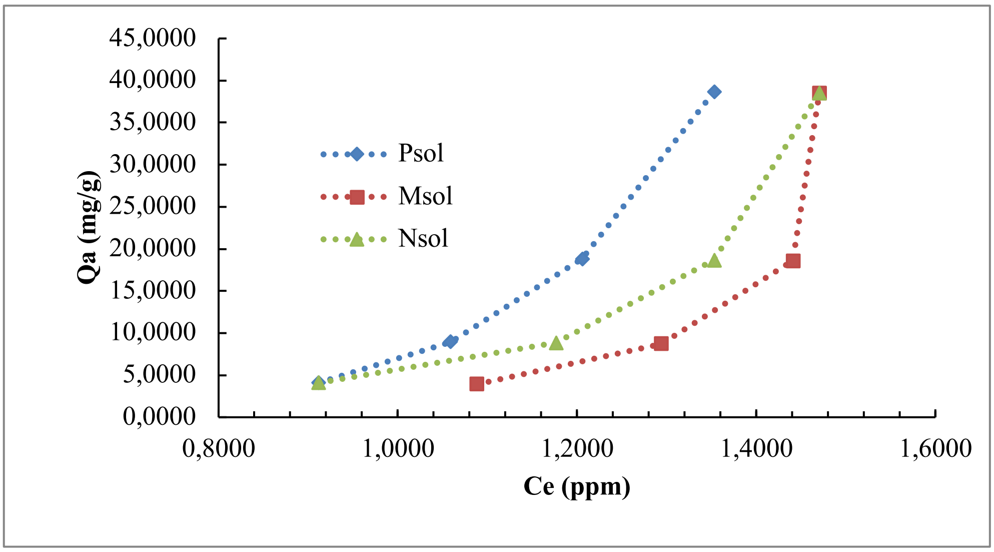


Figure 10. Adsorption Isotherms of Ivermectin on the soils (Psol, Msol and Nsol)

Isotherms of adsorption of IVR on the soils studied were compared on the basis of Langmuir and Freundlich models. The plots of the models of the adsorption isotherms of IVR on Psol, Msol and Nsol are shown in figure 11a, b and c respectively for the models of Langmuir and figure 12a, b and c for the model of Freundlich. The corresponding parameters are grouped together in the table 4 (Savci, 2015, OECD 106, 2000).

Table 4. Parameters of the Isotherms of the adsorption of the Ivermectin on soils (Psol, Msol and Nsol)

Isotherms	Parameters	Adsorbent		
		M sol	**N sol**	**P sol**
Langmuir $\frac{1}{Q_e} = \frac{1}{bQ_m}\frac{1}{C_e} + \frac{1}{Q_m}$ **Eq. (3)**	R^2	0.995	0.999	0.957
	Qm.cal (mg/g)	**-1.66**	**-2.98**	**-2.23**
	Qm.exp (mg/g)	38.52	38.52	38.64
	b	-	-	-
	R_L	-	-	-
Freundlich $Ln(Q_e) = \frac{1}{n}Ln(C_e) + Ln(K)$ **Eq. (4)**	R^2	0.908	0.948	0.998
	$1/n_f$	6.80	4.49	5.68
	n_f	0.14	0.22	0.17

With Ce: the residual concentration at equilibrium (mg.l^{-1}); Qm: the maximum adsorption capacity (characteristic of the formation of the monolayer of adsorbed molecules) (mg.g^{-1}); b: the thermodynamic constant of the adsorption equilibrium characteristic of adsorbent, depending on the temperature and the experimental conditions (mg.l^{-1}). K the capacity of the adsorbent (g.l^{-1}) And n: heterogeneity factor, with n> 1. The values of the correlation coefficients are very close to 1 for the two isotherms models examined (Table 4). However, the adsorbed quantity calculated by the Langmuir model for the three types of soil is negative; therefore, the determination of the parameters R_L and b of this model is therefore impossible. Similar result was obtained by Popova et al. (Popova *et al.*, 2013) when studying the sorption of Oxytetracycline, chlortetracycline, and Ivermectin on Yolo and Argonaut soils. Langmuir's model therefore does not describe the experimental adsorption data. In the case of the Freundlich isotherm, the values of K_F and those of 1/n indicate good sorption capacity (table 4). This indicates that the adsorption of Ivermectin on soils (Psol, Msol and Nsol) follows better the Freundlich model than that of Langmuir. So the sorption of IVR is probably accomplished in multilayers on heterogeneous surfaces. According to Freundlich coefficient K_F, affinity of the soils tested for IVR could be ranked as follows: Psol (6.70g/L)>Nsol (5.41 g/L)>Msol (1.94g/L). Studies have demonstrated that IVR residues bind tightly to soil (Halley *et al.*, 1989a); IVR has a K_{oc} of 12600 to 15700, depending on soil type, and is therefore classified as immobile, given it high binding affinity for organic matter and the low solubility in water (Halley *et al.*, 1989a). Other values of K_{oc} were

estimated to vary between 4000 and 25800 L/Kg while the K_F was estimated at 396 (Krogh et al., 2008) other authors have reported a value of K_F equal to were 77.7 L/Kg (Kali *et al.*, 2022).

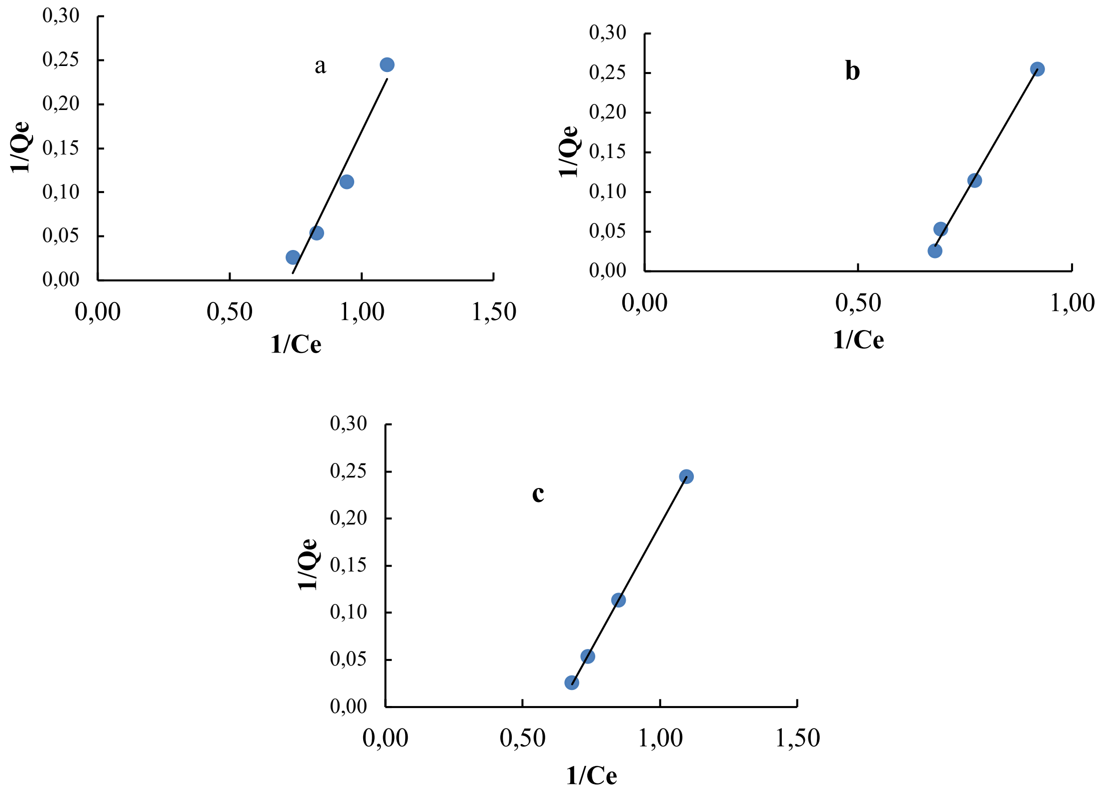


Figure 11. Isotherms of adsorption of IVR on soils a) Psol b) Msol and c) Nsol according to the Langmuir model

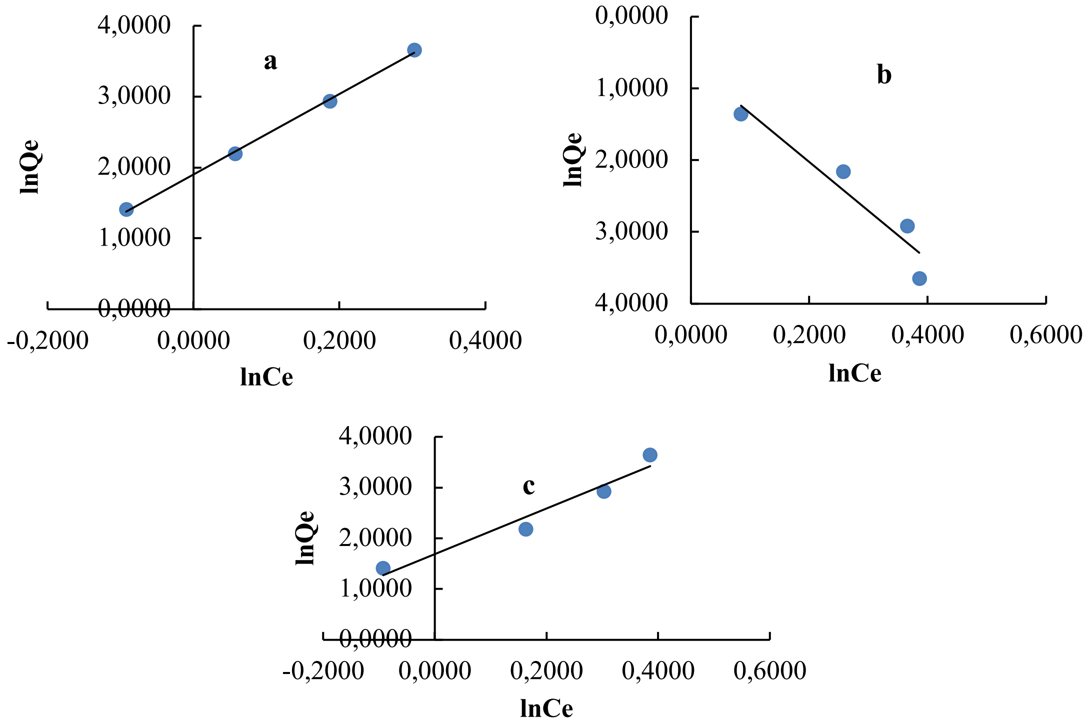


Figure 12. Isotherms of adsorption of Ivermectin on soils a) Psol b) Msol and c) Nsol according to the Freundlich model

The effect of soil structure was reported for other close pharmaceutical (Oxytetracycline and Chlortetracycline). The particle size has no effect on the adsorption of these pharmaceuticals, while it remains closely dependent of the organic matter. (Srairi et al., 2003)
Kd values of Oxytetracycline were found to be 420 and 1030 additionally, studies have shown that the antibiotics, Oxytetracycline and Chlortetracycline, demonstrate high sorption to soils regardless of particle size distribution. In sandy and sandy loam soil (OECD 312, 2004, Savci, 2015).
Table.5 shows K_{oc} deduced from percentage of organic matter of the soils studied according to the following equation Eq. **(7)** (Halley *et al.,* 1989a):

$$Koc = \frac{Kd \times 100}{\%OM \div 1.724} \qquad \textbf{(Eq.7)}$$

With:
Kd: is Freundlich coefficient
% OM is a percent organic matter;

1.724 is a factor to convert % OM to % oc (organic carbon) in the point of view of Howard, 1965 and Denis Baize 2012, based on the idea that carbon represent 58% of OM (Andaloussi et al., 2021).

Table 5. Estimated organic carbon coefficient for IVR

Soils	Psol	Nsol	Msol
Kd	6.69	5.41	1.94
%MO	3.8	3.6	3.4
Koc	102.11	87.24	33.16
Log Koc	2.01	1.94	1.52

These values are very low compared with values estimated by Halley et al. (Halley *et al.*, 1989a). In addition, these values are higher than 15 (>15), which corroborate the adsorptive capacities of the soils under study. This is in agreement with the assessment which classifies compounds with a Koc < 15 a being very mobile and those with a Koc > 4000 as being effectively non-mobile (Louise, 2009). This could be due to the involvement of other mechanisms such as cation exchange, cation bridging, surface complexation and hydrogen bonding (Tolls, 2001).
In an approach to assess the models used to evaluate and standardize the behavior of IVR and its analogues (Abamectin, Moxidectin, Doramectin), tests were carried out with 20 soils and sediments from Germany and Morocco (Gharb), the Kd ranged from 38 to 642 mL/g. The Kocs vary from 3.63 to 412. These values confirm the high affinity of these products for soils and sediments around the world. Based on the Freundlich model, the authors noticed a certain divergence with the model for soils with organic matter levels below 0.3%. This would be due to the composition of the organic matter and the lack of certain ligands responsible for hydrophobic or hydrophilic interaction (Heinrich et al., 2021).

3.3 Mass effect

In order to estimate the optimum quantity of soils to be added to the solution of IVR and its effect on the adsorption the experiments were carried out as previously described. Figures13a, b and c show that the adsorbed amount of IVR by the soils studied remain unchanged after varying the mass of adsorbent. This confirms the rapid reach of the maximum of adsorption reported earlier.

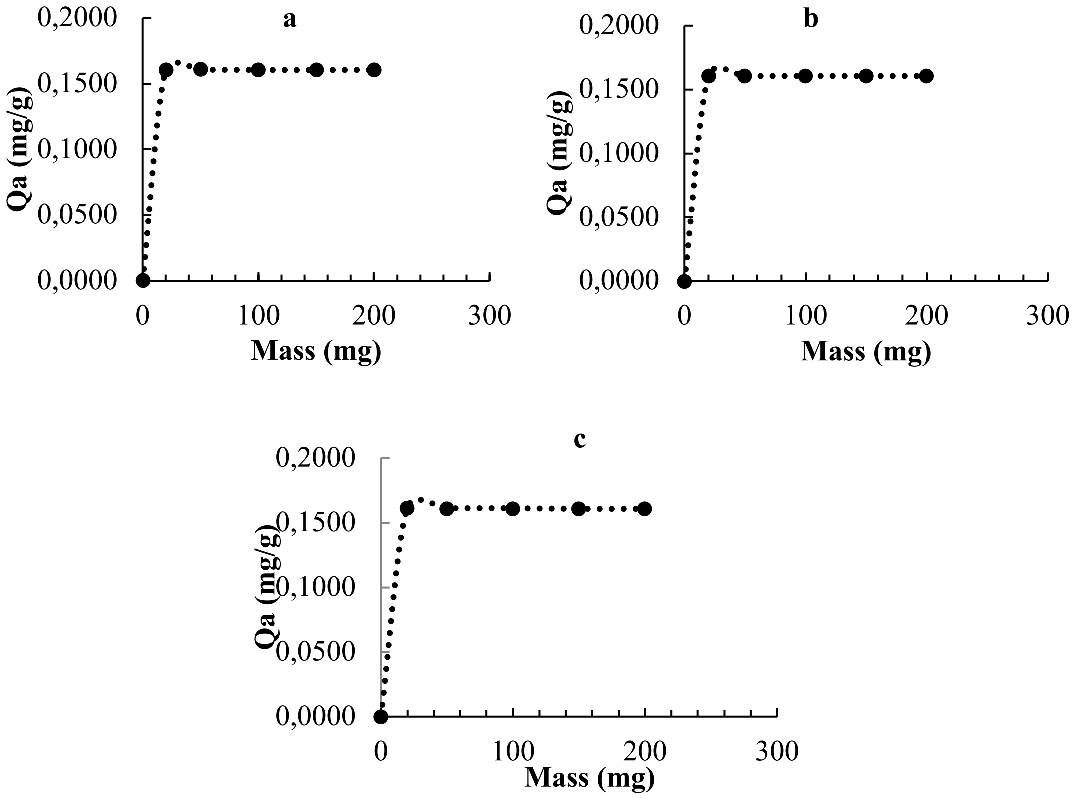


Figure 13. The effect of soil mass (Psol a, Msol b and Nsol c) on the adsorption of Ivermectin

3.4 pH effects

The experiments were carried out as previously described. The results illustrated in the figure 14 show that the adsorption rate of IVR is generally not influenced by variations in pH, which results in the pH of the solution having no effect on the adsorption of Ivermectin by soils.

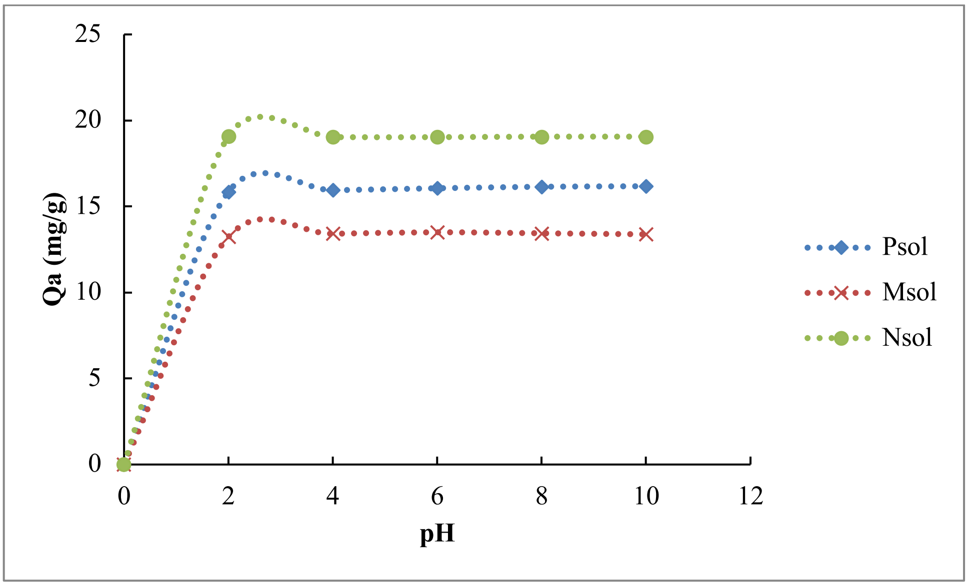


Figure 14. The pH effect on the adsorption of Ivermectin on the soils (Psol, Msol and Nsol)

3.5 Thermodynamic aspect

Temperature plays an important role in the adsorption of substances such as pesticides, dyes and metals on various solid surfaces. This could be reflected by an increase or decrease of the adsorption,

subsequent to an increase or decrease of the kinetic of the molecules in the solution. Gibbs equation (equations 8 and 9) is often used to disguish between chemisorption (ΔG° > de 40 KJoule/mole) and physisorption (Choumane, 2015).

$$\Delta G° = -R\ T\ Ln\ K_e \qquad \textbf{(Eq.8)}$$

$$K_e = (C_o - C_e)\ V/\ C_0\ m \quad = \quad Qe/Ce \qquad \textbf{(Eq.9)}$$

With:
Qe: the amount of IVR adsorbed
Co: Initial Concentration of the adsorbate
Ce: equilibrium Concentration of adsorbate
Ke: equilibrium Constant
ΔG°: free enthalpy (joule/mole)
T: absolute Temperature (K)
R: ideal gas constant (8.314 Joule/mole K)
In this study, the temperature was kept constant at 300 °K; Results of different parameters related to this equation are presented in table. 6.

Table 6. Values of the free enthalpy of the adsorption of the IVR by the different soils

Soils	**Ce (mg/L)**	**Qe (mg/g)**	**T (°K)**	**Ke (g/L)**	**ΔG° (j/mole)**
Psol	3.26	16.73	300	5.13	-4078.28
Msol	2.32	17.67	300	7.61	-5061.88
Nsol	3.32	16.67	300	5.02	-4024.21

Values of the free energy vary negatively between -4024.21 and -5061.88J/mole indicating a spontaneous process for the three soils as reported by other authors for other substances (Fayoud *et al.*, 2015, Choumane, 2015). However, the negative values of ΔG° indicate a physisorption process. This is not in agreement with previous study by Savci (Savci, 2015) who reported positive value of free energy with activated sludge. These could be due to low organic matter of the soils compared with sludge, allowing more interactions with sites prone for Van der Waals interactions than chemisorption.

3.6 Mobility in soils

Spectrophotometric analysis of 4 fractions of water collected (400 mL) from the 37 cm columns showed no detectable residue of IVR for all soils; this would reflect the expected strong retention of the product by the soil. To remedy to this constraint, the columns were replaced with small columns of 5 cm high to expect collecting residues in the fraction of water percolated.
The collection of percolated water was done by 7 fractions of 50 mL each and the results of the residue analyzes are presented in Table 7.

Table 7. Percentage of IVR residue detected in each percolate

Baches of 50 mL	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**% of elution**
P sol	0.64	0.39	0.20	0.16	0.10	0.05	0.00	**1.53**
M sol	0.65	0.43	0.20	0.13	0.09	0.04	0.00	**1.54**
N sol	0.70	0.44	0.20	0.13	0.10	0.04	0.00	**1.60**

As expected, total residues collected from the columns of the three soils are very low and similar. The percentages of IVR detected and vary from 1.53 to 1.60% of the amount of IVR introduced into the column. This confirms the very low mobility observed in the preliminary trials and the results reported by other authors.

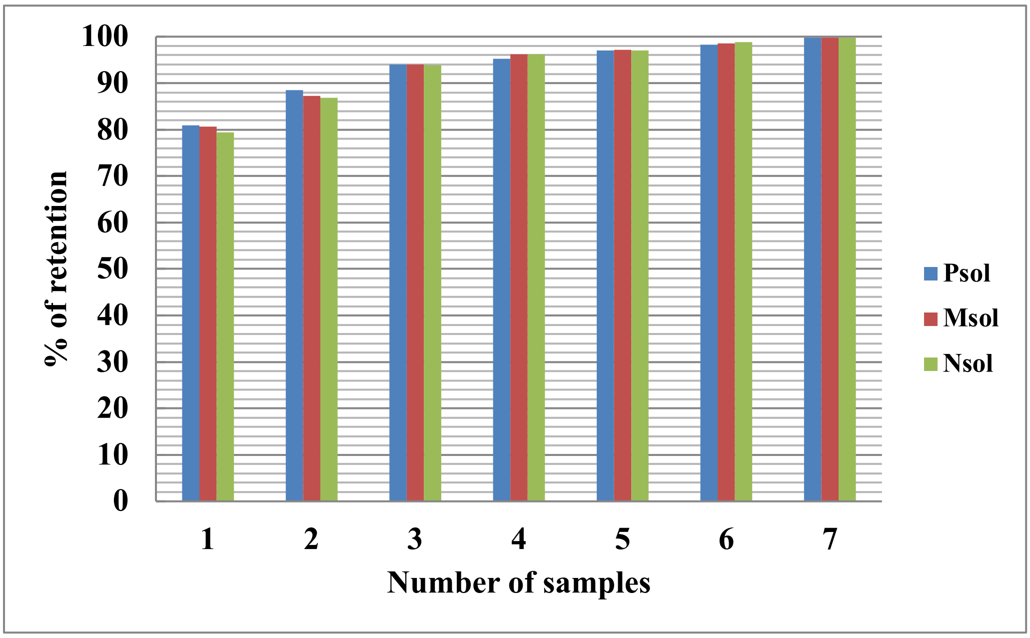


Figure 15. Retention rate of Ivermectin by the soils tested

Figure 15 translates the same behavior in terms of retention and shows that the IVR retention rates as a function of the number of samples of water collected. It appears that after the 7th fraction collected, the total residues retained approaches100%.of the amount introduced in the column.

This high retention may be due to the relatively high organic matter content in the soils studied. Indeed, the soils (Psol, Msol and Nsol) have a clayey and silty structure with percentages of organic matter greater than 3% (Table 2). The relatively high organic matter in the soils studied could be among the main factors behind the high retention recorded. This contribution has been mentioned by other authors on the basis of Koc that varies from 12600 to 15700 (Halley *et al.,* 1989a). On another hand, since IVR has a high binding affinity for organic matter and a low solubility in water (Halley *et al.,* 1989a, Gruber *et al.,* 1990); it is therefore classified as immobile**.** This feature could be similar to that reported for Avermectins by Gruber (Gruber et al., 1990). Actually, this author assessed that Avermectins are immobile especially in clayey and loamy soils. Another study of the mobility of pharmaceutical products in the terrestrial environment: adsorption kinetics of the macrocyclic lactone Eprinomectin in soils, by analyzing three types of soil with eight concentrations of this compound and therefore the Eprinomectin has been found to be relatively immobile in the environment when present in soils containing adequate amounts of organic matter and clay that possess numerous surface sites for binding of molecules and ions. In contrast, the drug is likely to be more mobile in soils that are low in clay and organic matter (Vassilis *et al.*, 2016).

Other authors like Kenaga have used the Koc parameter as an indicator of the leaching of chemical compounds through the soil and also indicates whether these compounds applied to the soil are more likely to enter the water by runoff in solution and point out that the chemicals with Koc> 1000 were described as immobile and those with Koc < 100 as mobile (Kenaga, 1980).

GUS Index (Groundwater Ubiquity Score)

In order to classify pesticides according to their leachability and to assess if they present a danger to groundwater. Gustafson developed a leaching risk index that was based on observations of groundwater contamination (Gustafson, 1989).

This index is based on the graphical examination formed by two properties of widely available pesticides: the half-life time in soil ($t_{1/2}$ soil) and the partition coefficient between soil organic carbon and water (K_{oc}). These properties have great power in distinguishing between mobile and immobile pesticides through the following GUS Index (Groundwater Ubiquity Score) calculation function:

$$GUS = \log_{10} (t_{1/2}\,soil)\,(4 - \log_{10} (K_{oc})) \qquad \textbf{(Eq.10)}$$

With:

$T_{1/2}$ in soil: half-life time of the substance DT50 (in days);

Koc: partition coefficient between soil organic carbon and water of the substance (L/kg) (Gustafson, 1989).

Based on the implementation of GUS equation and comparison with experimental results, it was found that the pesticides with GUS index higher than 2.8 are more common in groundwater and pesticides with GUS index lower than 1.8 are rarely found in water (Barriusu *et al.,* 1996). Therefore, Gustafson's GUS index is divided according to the GUS scale into three classes for the leachability of pesticides (Hayo *et al.,* 1998):

- Pesticides classified as mobile (GUS > 2.8);
- Pesticides classified as non-mobile (GUS < 1.8);
- Pesticides classified as "moderately mobile" (1.8 < GUS < 2.8).

Implementation of GUS in the cases of IVR is expressed as follows:

$$GUS = \log_{10} (14)\,(4 - \log_{10} (15700))$$

$$GUS = -0.22$$

With: K_{oc} = 15700 and $t_{1/2}$ soil = 2 weeks (14 Days) of Ivermectin in table 1.

From the GUS scale, it can be seen that the GUS index for IVR is less than 1.8; which could explains why the IVR is immobile and could not be detected in the percolated water from the columns.

Conclusion

This study has dealt with the residual effect of IVR in soils from Gharb region (Morocco). IVR was highly adsorbed in the studied soil. The affinity of the soil was ranked as follow: Msol (6.70 g/L) > Nsol (5.41 g/L) > Psol (1.94 g/L). Comparison of kinetic models showed that adsorption follows pseudo-second order model. Adsorption on the soil studied is well described by Freundlich model compared to Langmuir model though the high correlation coefficient obtained. The effects of different parameters such as contact time, mass of adsorbent, pH, and initial concentration were examined. No effect was observed related to variation of the mass of adsorbent or pH. The high affinity of the soils to IVR contributes to a rapid saturation of the soil that becomes non sensitive to any variation of physical-chemical parameters. Also, the process of adsorption of Ivermectin on the three types of soil is done spontaneously and would be in favor of physisorption mechanisms.

Regarding the mobility of IVR in the soils of the Gharb region, Ivermectin is immobile in the soils (Psol, Msol and Nsol). This can be explained by the strong interactions with the organic matter of the

soils studied, translated by the Koc adsorption coefficients. The IVR tends to remain localized in the first 5 cm of the ground. This immobile character of IVR was confirmed by GUS index that is bellow 1.8. This would reduce the risk of groundwater contamination; however, caution should be paid for surface water that could be contaminated by surface running water rejected mainly from cattle husbandry.

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