

Ammonium sorption by soils profile of semi-arid areas

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Abstract: The establishment of the ammonium (NH_4^+) sorption capacity by soil in the Sahel region of Tunisia is crucial for effective management of NH_4^+ in the region. However, the NH_4^+ sorption capacity for soils is not well developed. The aims of this study were to determine the NH_4^+ sorption capacity of soils and to generate that relates these capacities to soil properties. Air-dried samples soils collected at four depths, 0–25-, 25–60-, 60–90- and 90–120-cm from three sites in the Sahel region of Tunisia (Chott-Mariem, Enfidha and Kondar). Soil chemical, physical and mineralogical properties were analyzed. The kinetic sorption of NH_4^+ by the soils was investigated using batch experiments. The contact time to achieve the equilibrium condition was 300 min. The average amounts of NH_4^+ sorption on these soils varied from 5, 4 to 6, 35 mg.g^{-1} . The maximum adsorption ranked as: Kondar>Enfidha>Chott Mariem. Differences in NH_4^+ sorption were greatly influenced by soil organic matter, exchangeable cations (Ca^{2+} , K^+ and Mg^{2+}) and clay content. As far as the modeling is concerned, the kinetic sorption was fitted by the first order, second order kinetics and Elovitch model. Isotherm experiments were carried out by concentrations the following (0, 25, 50, 75, 100, 125, and 150 $\text{mg NH}_4^+ \text{L}^{-1}$). The equilibrium data was fitted with Langmuir and Freundlich isotherms. Comparison of the adjusted R^2 and RMSE for the two models indicated that the Langmuir model could adequately predict the NH_4^+ sorption process.

Keywords: Ammonium, semi-arid areas, sorption, soil properties, kinetic, isotherms.

I. Introduction

Ammonium (NH_4^+) is an inorganic ion form of nitrogen impurity. It is an essential nutrient for all living organisms. Although in most soils NH_4^+ can be the major source of nitrogen (N). It may also result from the mineralization of soil organic matter (SOM) [1]. The efficiency of N fertilizers can be significantly affected by the mobility of NH_4^+ essentially due to an increasing N uptake by crops from native soil N pools [2]. Ammonium is a usual subsurface pollutant that may result from different sources such as leakage from landfills, incorrect sewage systems and contaminated industrial sites, aquifer recharge with pretreated wastewaters, and fertilizer application [3]. High concentrations lead to the growth of algae and plants resulting in a reduction of dissolved oxygen and toxicity for aquatic organisms. In soil, NH_4^+ dynamics is affected by the process of sorption and desorption. These are important factors affecting the N availability for crops and for the protection of soil N supplies against leaching [4]. The amount of sorption and desorption of NH_4^+ depends on the fixation capacity of soils. This capacity can be determined by the complete saturation of fixing sites in soil with excessive amounts of NH_4^+ [5]. In fact, the NH_4^+ ions can be electro-statically adsorbed on soils surfaces [6]. On the basis of surface chemistry, soils can be divided into two groups with permanent and variable charges [7]. Soils with variable charges can have both positive and negative charges. The total amount of the variable charge differs because of mineral compositions and pH variation. Soils with positive charges can adsorb the major part of the applied fertilizers consisting of NH_4^+ . The NH_4^+ ion-exchange capacity varies depending on the presence of other cations in the solid and solution phases and on the initial NH_4^+ concentration [8]. NH_4^+ adsorption occurs by the ion exchange of NH_4^+ ions with sodium, potassium, magnesium, and calcium ions at cation-exchange sites. The electrostatic energy between NH_4^+ or K^+ and the negative charges in the crystal sheets is greater than the hydration energy of these cations. Therefore, they easily lose hydration water and are placed in the interlayer holes. The silicate layers collapse, and consequently the trapped NH_4^+ and K^+ between sheets will be non-exchangeable [4]. Wang and Alva [9] by studying the effect of soil texture on NH_4^+ absorption found that clay soils were more capable to adsorb NH_4^+ than sandy soils. The (2:1) clay minerals type including illite, vermiculite, and montmorillonite, has the greatest NH_4^+ -retention capacity. The negative charges of these minerals may be balanced by absorbing cations such as NH_4^+ and K^+ . Both ions can be held in the ditrigonal spaces in the basal oxygen plane of (2:1) clay minerals due to having the same ionic radius and low hydration energy [1]. NH_4^+ sorption in agricultural and forest soils has been widely investigated [9]. Considering the intensive application of N fertilizers in semi-arid areas of Tunisia, we have conducted this study to improve the knowledge about NH_4^+ sorption using results from kinetics and isotherms data.

II. Material And Methods

Site description

The ammonium sorption research was conducted with soils from three sites of the semi-arid areas of Tunisia: Chott Mariem (35°54'N10°36'E), Enfidha (36°08'N10°22'E) and Kondar (35°55'N10°17' E). The climate is moderate in the winter and hot in the summer, with mean annual temperature of 23°C, and mean annual precipitation of 300 mm. The soil (0–25-cm) is fine sandy loam (Isohumic soils) at Chott Mariem, clay soil (Calcic-magnesian) at Enfidha and Kondar (Solonetz) [10].

Physicochemical analysis

Triplicates soil samples were randomly collected at four depth, 0–25-, 25–60-, 60–90-, and 90–120-cm, air-dried, sieved (<2 mm) and stored until analysis. The soils were classified as Isohumic soils for Chott Mariem, calcic-magnesian for Enfidha, and solonetz for Kondar [10]. Soil pH was determined in a 1:2 soil: water suspension [11]; organic C (OC) by the wet oxidation method [12]; particle-size distribution by the pipette method [13]; and calcium carbonate equivalent (CCE) by the BaCl₂ extraction method [14]. Mehlich-III P, Ca, Mg, Fe, Al, Cd, Cu, Mn, were determined by equilibrating 2.5 g of air-dried soil with 25 mL of Mehlich-III extracting solution for 5 min and filtering through Whatman No. 40 filter paper. Concentrations of the various elements in the extracts were determined by inductively coupled plasma optical emission spectrophotometer (CP-OES, Perkins Elmer, Model 4300DV). Soil N-NO₃⁻ and N-NH₄⁺ concentrations were analyzed using the steam distillation method.

Mineralogy analysis

The quantitative mineralogical analysis was extracted from the powder XRD data using an internal standard for each mineral [16]. The clay fraction was quantified, after purification, and based on a pure, standard clay mineral [17].

Experimental sorption study

The batch sorption experiments were carried out in 250-mL Erlenmeyer flasks where 1 g of each soil sample and 100 mL of the NH₄⁺ solutions prepared with NH₄Cl were added in presence of 0.01 M CaCl₂ solution. The Erlenmeyer flasks were subsequently capped and agitated in an isothermal shaker at 100 rpm and 20±2° C to achieve equilibration at 300mn. The pH of all solutions is that the initial soil. After each 15 min, 5mL of solution was sampled from each flask, centrifuged at 2800 (g) for 10 min and the supernatant immediately analyzed for NH₄⁺ using the double beam UV–vis spectrophotometer (Shimadzu, Model UV 1601, Japan) at 668 nm. The amount of sorption at equilibrium, Q_e (mg.g⁻¹), was calculated by Eq(1):

$$Q_e = \frac{(C_e - C_0) \times V}{M}; \text{ Where } C_0 \text{ and } C_e \text{ (mg.L}^{-1}\text{) are the liquid-phase concentrations of NH}_4^+ \text{ at initial}$$

and equilibrium, respectively; V is the volume of the solution (L) and M is the mass of dried soil (g).

Kinetics modeling

Different models have been proposed to investigate the kinetic behavior of sorbents and examine the rate controlling the process. Traditionally one has to choose between the first and the second pseudo order. Recently progress has been made due to the availability of powerful nonlinear methods and the introduction of fractal concepts in complex reactions. In complex systems which or this aim, the classic models namely, the pseudo first-order, pseudo second-order rate equation model and Elovitch model were used in this paper.

The pseudo-first-order: The rate equation given by Lagergren, [18] is generally described by the following

equation (Eq2): $\frac{dq}{dt} = k_1(q_e - qt)$. After integration by applying the conditions, q_{t=0}=0 and at t=t, q_t=q_t,

Eq. (2) becomes (Eq3): $\log(q_e - qt) = \log(q_e) - \frac{k_1}{2,303} \times t$; Where k₁ is a constant and q_e is the amount of

NH₄⁺ sorbed at equilibrium in mg.g⁻¹. The constants k₁ and q_e can be calculated using the slope and intercept from the plot of log (q_e-q) versus time (t).

Pseudo-second-order model: The pseudo second-order kinetic model is expressed as follows Eq(4):

$\frac{dq}{dt} = k_2(q_e - qt)^2$. Integrating equation Eq (4) for the boundary conditions t = 0 to t = t and q_t = 0 to q = q_e

gives $\frac{t}{qt} = \frac{1}{k_2 qe^2} + \frac{t}{qe}$; Where: k_2 is the second-order rate constant ($\text{g mg}^{-1} \text{min}^{-1}$). By plotting t/q_t versus t in a linear relationship, values of k_2 and q_e were calculated from the intercept and slope of the plots.

Elovich equation: The Elovich equation was the third model used and can be expressed as: $\frac{dq_t}{dt} = \alpha e^{-\beta q_t}$, Eq (5); Where α is the initial adsorption rate ($\text{mg g}^{-1} \text{min}^{-1}$) and β is the desorption constant (g mg^{-1}). To simplify the Elovich equation, we assumed $\alpha\beta t \gg 1$ and applied the boundary conditions $q_t=0$ at $t=0$ and $q_t=q_t$ at $t=t$. Eq (5) then gives: $q_t = \left(\frac{1}{\beta}\right) \ln(t+t_0) - \left(\frac{1}{\beta}\right) \ln t_0$; where $t_0 = \frac{1}{(\alpha\beta)}$. If t is much larger than t_0 , this can be further simplified to: $q_t = \left(\frac{1}{\beta}\right) \ln(\alpha\beta) + \left(\frac{1}{\beta}\right) \ln(t)$, Eq (6). A plot between q_t versus $\ln(t)$ yields a linear relationship with a slope of $\left(\frac{1}{\beta}\right)$ and an intercept of $\left(\frac{1}{\beta}\right) \ln(\alpha\beta)$. The term $\left(\frac{1}{\beta}\right)$ indicates the number of sites available for adsorption.

Isotherms modelling

The study of equilibrium behavior of sorbent is necessary to design and optimize the adsorption systems [19]. The correlation between the adsorbent concentration in the liquid phase and the adsorption capacity at equilibrium time is presented by isotherm models. Among many isotherms investigating the adsorption mechanism, Langmuir [20] and Freundlich [21] are the most common isotherm models. In this study, the equilibrium behavior of the sorbent during ammonium ion adsorption was investigated by Langmuir and Freundlich models at different earlier concentrations.

Langmuir equation

The Langmuir isotherm is based on monolayer coverage of adsorbent homogenous surface with the constant adsorption heat for all active sites that is given as Eq. (4): $Q = Q_{\max} \times \frac{k_1 \times C}{1 + k_1 \times C}$; Where Q ($\text{mg NH}_4^+ \text{kg}^{-1}$) is the adsorbed NH_4^+ onto the soil after 24-h contact, Q_{\max} ($\text{mg NH}_4^+ \text{kg}^{-1}$) is the NH_4^+ sorption maximum; k_1 ($\text{NH}_4^+ \text{mg.L}^{-1}$) is the binding energy of NH_4^+ , and C ($\text{mg NH}_4^+ \text{L}^{-1}$) is the equilibrium NH_4^+ concentration in solution.

Freundlich equation

The linear form of Freundlich model defined by $Q = k_F \times C^n$; Where Q ($\text{mg NH}_4^+ \text{kg}^{-1}$) is the adsorbed NH_4^+ onto the soil after 24h contact, k_F is a coefficient, C (mg L^{-1}) is the equilibrium NH_4^+ concentration in solution, and n is a coefficient introducing non-linearity.

Statistical analysis

Non-linear regression techniques were applied to the sorption data using NLIN procedure [22]. Sorption was characterized by fitting Eqs. (1) and (2) to the plot of adsorbed NH_4^+ against equilibrium NH_4^+ concentration in solution. The fit of the regression curve was evaluated using the adjusted R^2 to determine how well the curve explains experimental data variation and the root mean square error (RMSE) which estimates the variation, expressed in the same units as the data, between theoretical and experimental values. This parameter is

defined by the following formula: $\text{RMSE} = \left[\sum_{i=1}^n \left(\frac{Q_{\text{the}} - Q_{\text{exp}}}{n} \right)^2 \right]^{1/2}$, where: Q_{the} and Q_{exp} are simulated and

observed values, respectively. The RMSE tests the accuracy of the model, which is defined as the extent to which simulated values approach a corresponding set of measured values (Daroub et al., 2003) [23].

III. Results And Discussion

Physicochemical analysis

The main soil properties thought to influence NH_4^+ sorption and movement are indicated in Table 1. All of the different samples were alkaline for all depths with the pH generally above 8. The texture for the Chott Mariem area varied with depth, and ranged from a fine sandy loam to clay. Soil texture Kondar for the varied to

clay a heavy clay. Finally, in the profile texture soil area of Enfidha, only heavy clay texture soil was determined at different horizons.

Table 1. Soils characteristics

Dept(cm)	Chott-Mariem area				Enfidha area				Kondar area			
	0-25	25-60	60-90	90-120	0-25	25-60	60-90	90-120	0-25	25-60	60-90	90-120
pH (H ₂ O)	8.12	8.41	8.56	8.54	8.26	8.14	7.97	7.87	8.66	8.86	8.35	8.12
OM (%)	1.89	1.42	3.61	4.66	3.48	3.18	3.19	3.08	7.36	7.13	5.68	1.89
P(mg/kg)	93.68	20.90	4.12	4.99	4.48	2.19	3.70	3.79	1.98	1.53	1.27	1.91
Ca(mg/kg)	5450	5508	5874	5450	10026	9495	7885	11360	17784	10108	12786	20337
Al(mg/kg)	76	87	72	51	230	159	108	198	34	19	14	34
K (mg/kg)	491	299	135	106	294	310	298	376	143	129	160	234
Fe(mg/kg)	33	24	9	3	41	41	45	44	12	19	30	31
Mn(mg/kg)	410	433	356	461	668	774	717	841	680	963	1000	966
Clay	12.8	24.4	30.5	25.8	63.3	76.1	78.8	77.5	58.6	56.8	51.5	71.8
sand	49.2	60.4	59.5	59.1	20.7	13.9	12.2	10.5	28.6	26.8	46	24.2
Silt	38	15.2	10	15.1	16	10	9	12	12.8	16.4	2.5	4
Texture	Fine sandy loam	Loam sandy clay	clay	Loam sandy clay	Clay	Heavy clay	Heavy clay	Heavy clay	Clay	Clay	Sandy clay	Heavy clay

Clay content in particular can affect soil behaviour, fertility, water and nutrient holding capacities as well as plant root movement. The Enfidha soils with their high clay content would probably hold more water and nutrients than the two other soils. The organic matter (OM) content for the different soils horizons was highly variable between the various areas and horizons. For Enfidha soils, the OM content was similar for all depths, with a mean of 3.16%, which was relatively high compared to the other soils. This is likely due to migration of OM to deeper horizons and its incorporation with the particle size of clay under the action of microbial activity [24]. In the Chott-Mariem soils, the majority of OM accumulated at depth, primarily between 60 and 120 cm. By contrast, the soil profile from the Kondar site contained very high rates of OM in the surface horizons (i.e. 0-25 cm and 25-60 cm), which decreased with the depth. In general the distribution of level of OM is influenced by different factors such the amount of OM and the soil texture, especially clay content [25]. The amount of exchangeable cations also differed markedly between the soils. The Ca content was particularly different and varied between less than 6 mgkg⁻¹ dry weight in the surface horizon for the Chott-Mariem profile to more than 20 mgkg⁻¹ dry weight for the deeper horizon from the Kondar profile. The values for the soils were high and in all instances increased with depth. By contrast, available P, in the two of the three soils was low and in all profiles soil P decreased with depth. The inverse can be seen for other exchangeable cations such K⁺ and Fe²⁺ where concentrations were moderate and decreased with increasing depth. For the other ions there were no distinct patterns in terms of the amount and distribution within the different horizons of the soil profile.

Mineral analysis

The distribution of minerals in each profile depicted in Table 2 can be described in the following way: for the soil profile of Chott-Mariem, one can observe a relative homogeneity of the proportions in quartz in the all layer, increasing of calcite in the deep layer and different abundance of the kaolinite, illite and chlorite. For the Enfidha soil profile, one observes a relative homogeneity of the distribution of the proportions in kaolinite, quartz, calcite, smectite in the all horizons and different abundance of illite and chlorite. Finally for the Kondar soil profile, the data suggest a preponderance of quartz, calcite in all the horizons and then become less abundant in the deep horizons. The smectite is detected with stable values in all layers but the kaolinite, illite and chlorite show an irregular abundance.

Table 2. Mineralogical composition of the different soils profiles

Area	Depths	Identification of mineralogy					
		Kaolinite	Quartz	Calcite	Smectite	Illite	chlorite
Chott-Mariem	0-25cm	+	+++	+	-	-	-
	25-60cm	-	+++	+	+	-	-
	60-90cm	+	+++	+	+	+	-
	90-120cm	+	+++	++	+	+	+
Enfidha	0-25cm	+	+++	++	+	-	+
	25-60cm	+	+++	++	+	+	-
	60-90cm	+	+++	++	+	+	-
	90-120cm	+	+++	++	+	+	+
Kondar	0-25cm	-	+++	+++	+	-	-
	25-60cm	+	+++	+++	+	-	+
	60-90cm	+	+++	+++	+	+	+
	90-120cm	+	++	++	+	+	+

+++ Abundant, ++ moderately abundant, + poorly abundant

Sorption kinetics of NH_4^+

The effect of the contact time on NH_4^+ ion sorption is shown in Fig. 1.2. and 3.

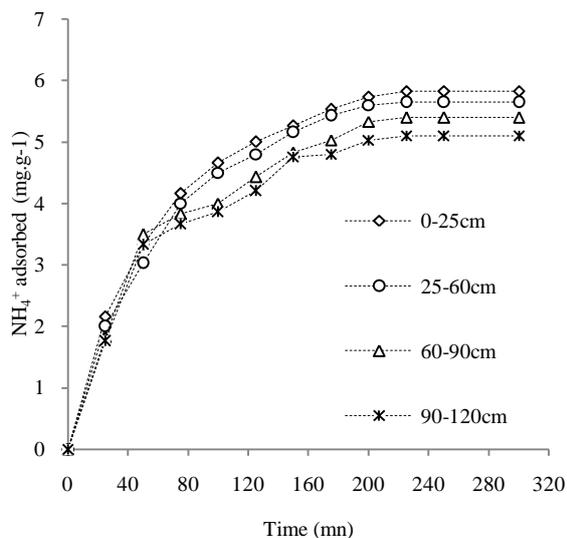


Fig.1. Effect of contact time in adsorption (NH_4^+) by the soil of Chott Mariem.

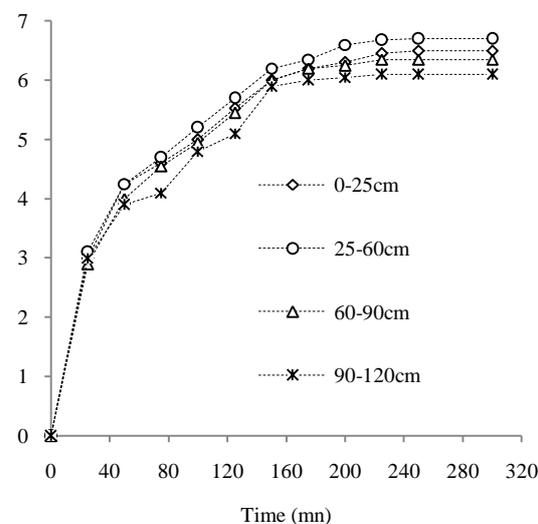


Fig.2. Effect of contact time in adsorption (NH_4^+) by the soil of Enfidha.

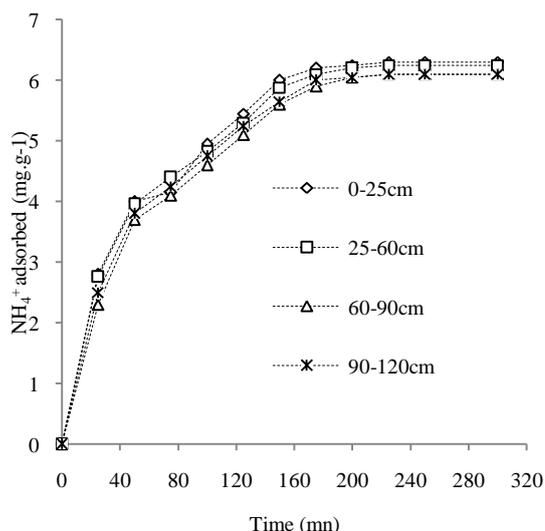


Fig. 3. Effect of contact time in adsorption (NH_4^+) by the soil of Kondar.

The increment of the contact time leads to the increasing of the NH_4^+ ion sorption by the soil solution. As it can be seen, the increase in NH_4^+ sorption capacity is rapid within the first 60 min. It can be due to increase diffusion in the pores during the first 60 min [26]. In the course of time, pores are occupied due to NH_4^+ ion sorption causing the increase of the NH_4^+ ion sorption capacity. But, with the increase of contact time, there is a decrease of the driving force during the mass transfer process and consequently the NH_4^+ sorption decrease slowly until 120 min and finally reaches a constant value after approximately 300 min which is considered as the equilibrium time [26]. Zhu [27] reported that the sorption of the NH_4^+ decreased with time until equilibrium was approached. Ranjbar [8] indicated that the sorption NH_4^+ in calcareous soils decreases after 90mn. Weatherley and Miladinovic [28] indicated that 50–59 % of applied NH_4^+ was adsorbed during a short time in laboratory and field experiments. The amount of sorption by different soil profiles for 0-25; 25-60; 60-90 and 90-120 cm depths are in order of 5,4 ; 5,3 ; 5,1 and 5,25 mg.g^{-1} , in order of 5,83; 5,6; 5,4 and 5,1 mg.g^{-1} and in order of 6,35; 6,25; 6,1et 6,1 respectively from the soil profile of Chott-Mariem, Enfidha and Kondar. Moreover sorption is a rapid process due to the increased level of soluble and NH_4^+ ions. The maximum amount of sorption was observed in soil profile of Kondar. The lowest and the highest values were measured in the deeper (90-120cm) and surface (0-25cm) soil layer respectively.

Modeling kinetics sorption

The parameters of kinetic models are listed in Table 3. Based on the highest R² and the lowest SE and Q, it can be revealed that the pseudo-second order model can describe kinetic behavior. R² values in this model are higher and the calculated sorption capacities are in agreement with experimental values. This result is in accordance with reported results by Liu et al., [29].

Table 3 : Modelling kinetics parameters.

	Profondeur	Premier ordre			Second ordre			Elovitch		
		R ²	Qe (mg/g)	k	R ²	Qe(mg/g)	k	R ²	α(mg.g-1.min ⁻¹)	β(g.mg-1)
Chot	0-25cm	0.997	5,877	0.037	0.997	7,166	0.0002	0.98	0.059	2.243
	25-60cm	0.998	5,769	0.035	0.994	7,120	0.0002	0.984	0.057	1.903
	60-90cm	0.983	5,395	0.037	0.989	6,571	0.0002	0.982	0.064	2.058
	00-120cm	0.986	5,108	0.039	0.989	6,195	0.0003	0.980	0.0694	2.070
Enfidha	0-25cm	0.980	6,3428	0.040	0.987	7,564	75.644	0.983	0.060	3.168
	25-60cm	0.983	6,2505	0.041	0.992	7,435	0.0002	0.988	0.061	3.269
	60-90cm	0.989	6,182	0.036	0.993	7,543	0.0002	0.987	0.056	2.276
	00-120cm	0.989	6,142	0.039	0.993	7,379	0.0002	0.987	0.060	2.800
Kondar	0-25cm	0.979	6,384	0.044	0.993	7,517	0.0003	0.992	0.063	3.988
	25-60cm	0.980	6,624	0.043	0.993	7,830	0.0002	0.992	0.060	3.852
	60-90cm	0.984	6,32	0.043	0.993	7,490	0.0003	0.989	0.062	3.618
	00-120cm	0.968	6,087	0.043	0.981	7,162	0.0003	0.983	0.066	3.719

Effect of initial NH₄⁺ concentration on NH₄⁺ sorption

Since that the initial NH₄⁺ concentration in solution provides an important driving force to overcome mass transfer limitations of NH₄⁺ between aqueous and solid phases, a higher initial NH₄⁺ concentration will enhance the sorption process. The effect of initial NH₄⁺ concentration on NH₄⁺ sorption for all soil depths was studied in the following concentrations (0,25, 50, 75, 100, 125, and 150mg NH₄⁺ L⁻¹) in presence of 0.01 M CaCl₂ solution. Figs. 4.5 and 6 illustrate the change of the equilibrium sorption capacity of soil samples with different initial NH₄⁺ concentrations. It was showed that the amount of sorbed NH₄⁺ at equilibrium enhanced with increasing initial NH₄⁺ concentration for all soil horizons, although rates differed according to the soil layer. In fact, the increase of concentrations at 25 to 150 mg NH₄⁺ L⁻¹, enhance the capacity sorption by the soil profile of area-Chott Mariem at 0.63 to 6.63; at 0.64 to 6.5; at 0.63 to 6.31 and 0.63 to 6 (mg.g⁻¹) from 0-25; 25-60; 60-90 and 90-120 depths respectively. For the soil profile Enfidha area, sorption increases from 0.34 to 6.47; from 0.34; from 0.31 to 6.43; from 0.34 to 6.07 (mg.g⁻¹) from 0-25; 25-60; 60-90 and 90-120 depths respectively. Finally for the soil profile area-Kondar, sorption also increased from 0.63 to 6.07; from 0.64 to 6.43; from 0.63 to 6.43 and 0.63 to 6.47 (mgkg⁻¹) from 0-25; 25-60; 60-90 and 90-120 cm depths respectively. NH₄⁺ sorption increased linearly with increasing concentrations of NH₄⁺ added in each soil. With the increase of NH₄⁺ concentration in solution, the sorption capacity of the NH₄⁺ ion also increases possibly because of complete substitution of other cations by NH₄⁺ ions. Indeed, it is noted that for the three soils profiles, sorption is higher in deep horizons that surface horizons.

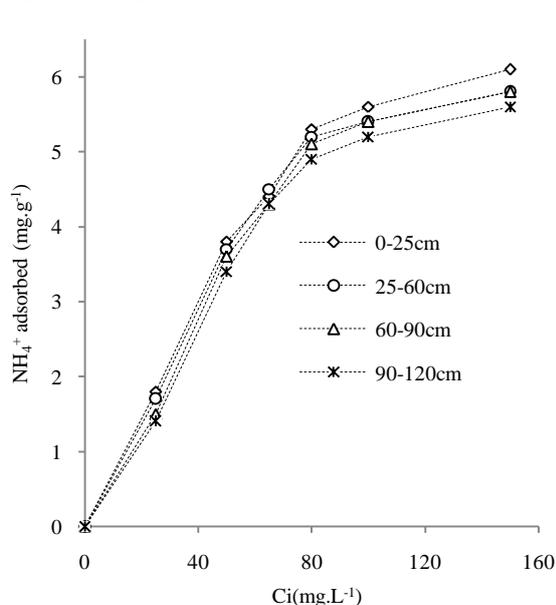


Fig.4. Effect of initial concentration on NH₄⁺ adsorption by Chott Mariem soil

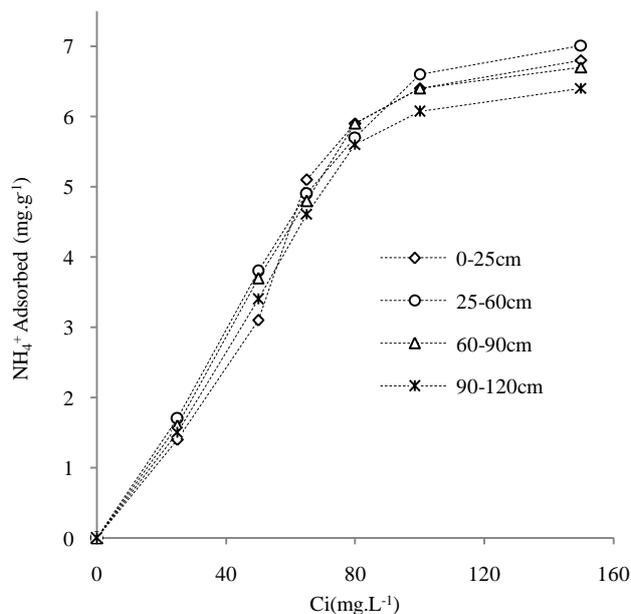


Fig.5. Effect of initial concentration on NH₄⁺ adsorption by Enfidha soil

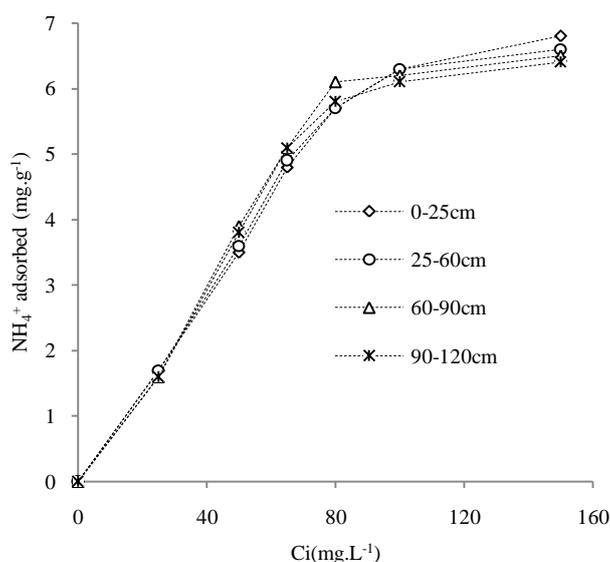


Fig.6. Effect of initial concentration on NH_4^+ adsorption by Kondar soil

Effect of substrate physicochemical properties on NH_4^+ adsorption

The results of physico-chemical and mineralogical showed in the Tables 1 and 2 reported that sorption of NH_4^+ had positive and negative correlation with some soils compositions. The maximum amount of strongly sorption NH_4^+ was observed in soil profile of Kondar area, which had the highest capacity exchange cation (CEC) and clay content. For soil Chott Mariem, the amount of NH_4^+ adsorbed decreases with an increase in calcium content in the different profile soil layer. However for the soil (Enfidha), we note that the retention of NH_4^+ decreases with soil depth and that this decrease was accompanied by a reduction in organic matter content and clay fraction. Wang et al., [7] show that the sorption of NH_4^+ is influenced by the addition of calcium ions. Ranjbar et al., [31] reported the crucial effect of Ca in the adsorption of NH_4^+ by calcareous soils. Others researchers have indicated that NH_4^+ sorption capacity remarkably depends on the degree of K^+ saturation of the interlayers of 2:1 clay minerals. High concentration of K^+ in soil solution results in saturation of interlayer spaces with K^+ and, to a smaller extent, with NH_4^+ ions [32]. The presence of NH_4^+ and K^+ may change the amount of sorption due to the competition for sorption sites. Kwok and Loh, [33] found that addition of K^+ before NH_4^+ caused a decrease in NH_4^+ sorption. Whereas Cui et al., [32] reported that pre-application of K^+ increased NH_4^+ sorption. Korkusuz et al., [34] indicated that NH_4^+ sorption was significantly greater in soils containing low contents of exchangeable K^+ compared with soils having a high degree of K^+ saturation. Sarioglu, [35] indicated that high application of K^+ caused no release of adsorbed NH_4^+ , whereas low addition of K^+ resulted in noticeable release of this fraction. Another hand Zhang et al., [4] found a positive correlation between amount of sorption NH_4^+ and soil clay content. Ranjbar et al., [8] found that NH_4^+ adsorbed was greater in clay soils than sandy soils. Furthermore, Nieder and Benbi [36] indicated that NH_4^+ content sorption varied from 10 to 90 mg kg⁻¹ in coarse-textured soils, 60 to 270 mg kg⁻¹ in medium-textured soils, and 90 to 460 mg kg⁻¹ in fine textured soils. Gouveia and Eudoxie [37] suggested that the saturation of exchangeable sites with NH_4^+ leads this ion to be placed in the interlayer spaces of clay minerals until all available fixation sites are occupied. The large internal surface area of 2:1 expanding clay minerals involved in fixation may be responsible for an abundance of both strongly and weakly adsorbed NH_4^+ sites [38]. Due to the equilibrium between weakly and strongly adsorbed pools, NH_4^+ ions transfer from the clay edges into interlayer spaces over time Gouveia and Eudoxie [37]. Indeed, the clay mineralogy had an important role in the adsorption NH_4^+ ions. Ranjbar et al., [31] indicated that the sorption of NH_4^+ strongly related on clays 2: 1, such as smectites that are prevalent in our soils after their identification by X-rays. Sprynskyy et al., [39] revealed that NH_4^+ sorption capacity of illite was greater than that of montmorillonite. In contrast, Feigenbaum et al., [8] signaled that along with montmorillonite, is a high-fixing smectite due to the isomorphous substitution in the tetrahedral layer. Kaolinite as one of the 1:1 clay minerals is unable to adsorb NH_4^+ ions due to the hydrogen bonds, which prohibit the expansion of interlayer spaces.

Adsorption Equilibrium and Isotherms

Ammonium sorption and equilibrium solution NH_4^+ concentration increased linearly with increasing amounts of NH_4^+ added in each soil. With the increase of NH_4^+ concentration in solution, the adsorption capacity of the NH_4^+ ion also increases possibly because of complete elimination of other cations by NH_4^+ ions. Both

Freundlich and Langmuir isotherms were used to fit the NH_4^+ adsorption by the different soils in this study. The parameters of both empirical equations of Langmuir and Freundlich are given in Table 4.

Table 4 : Modelling isotherms parameters

	Profondeur	Qmax (mg/g)	R ²	Langmuir			Freundlich			
				Qe (mg/g)	kl	RMSE	R ²	Qe (mg/g)	1/n	RMSE
Chott mariem	0-25cm	6,11	0,99	6.821	0.110	0,11	0,98	2.458	0.211	0,59
	25-60cm	5,857	0,99	6.559	0.112	0,11	0,97	2.486	0.198	0,57
	60-90cm	5,867	0,99	6.672	0.093	0,13	0,98	2.225	0.223	0,62
	90-120cm	5,687	0,99	6.54	0.083	0,14	0,97	2.066	0.231	0,63
Enfidha	0-25cm	6,82	0,98	7.760	0.097	0,13	0,84	2.558	0.228	0,62
	25-60cm	7,013	0,98	8.332	0.089	0,18	0,96	2.449	0.252	0,65
	60-90cm	6,78	0,97	7.946	0.099	0,17	0,94	2.606	0.229	0,61
	90-120cm	6,42	0,97	7.794	0.073	0,21	0,93	2.152	0.257	0,66
Kondar	0-25cm	6,86	0,96	8.321	0.074	0,21	0,94	2.187	0.271	0,68
	25-60cm	6,632	0,97	7.723	0.102	0,16	0,94	2.620	0.221	0,6
	60-90cm	6,579	0,97	7.284	0.164	0,1	0,94	3.273	0.167	0,5
	00-120cm	6,412	0,97	7.225	0.140	0,12	0,94	3.035	0.179	0,52

According to this Table it can be shown that application of the Langmuir equation indicates that the sorption phenomenon was adequately described by this isotherm. It can be provided a strong fit adjusted R^2 ($R^2 \geq 0.97$) and weakness values of RMSE for all layers of different profiles except in the layer of (0-25cm) of Kondar profile which it recorded a low value of $R^2 = 0.96$ and a high value $\text{RMSE} = 0.21$. The value of k_L (Lmg^{-1}) parameter of the Langmuir model is the constant representing the affinity of sorbate to sorbent. However, k_L changed with depth, which suggests that variation availability of inorganic sites for NH_4^+ binding. Comparison of these values with k_L parameter of the Langmuir model in this study reveals that the sorption affinity of NH_4^+ to samples soil Chott Mariem is lower than the affinity of Enfidha and Kondar. Both the Q_{max} and binding energy (k_L) values indicated that NH_4^+ sorption capacity as suggested by the population of sites in the low equilibrium NH_4^+ . High k_L values observed in this experiment show that the tenacity of ammonium sorption is greater at low NH_4^+ equilibrium concentrations. However, as shown in Table 4 the Freundlich model also could not describe the sorption of P onto soil samples acceptably, because this model also assumes a different behavior for the sorption of a NH_4^+ onto soil samples and its corresponding R^2 and RMSE values in Table 4 concurred with this result. Furthermore, the value of Freundlich exponent $1/n$ was greater than 0.16., indicates an inadequately adsorption.

Comparing the two equations it may be concluded the Langmuir model showed a better fit to the data than the Freundlich model. Although the Freundlich isotherm provides the information about the surface heterogeneity and the exponential distribution of the active sites and their energies, it does not predict any saturation of the surface of the sorbent by the sorbate. Whereas the Langmuir isotherm fits the experimental data well may be due to homogeneous distribution of active sites on the samples soils surface; since the Langmuir equation assumes that the adsorbent surface is energetically homogeneous. Nearly similar results have been reported in the literature [40, 41] for Langmuir and Freundlich models.

IV. Conclusion

The results of this study indicated that soil properties, including pH, exchangeable cations, CEC, and amounts of sand and clay, significantly influenced the sorption NH_4^+ by soils. The maximum sorption capacity of ammonium was obtained at profile soil of kondar 6, 35mg.g^{-1} . The kinetic data followed the pseudo-second-order kinetic model. Another hand there was a linear relationship between NH_4^+ concentration in solution phase and adsorbed NH_4^+ on solid phase as initial concentration of NH_4^+ increased. Langmuir and Freundlich isotherms were applied to test the equilibrium data. Langmuir isotherms showed a good agreement with the equilibrium data in various concentrations, thus showing that this adsorption is carried out homogeneously and in a monolayer.

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