Research Article

Nitrate Sorption in an Agricultural Soil Profile

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Increasing concentrations of NO_3^- in surface water and groundwater can cause ecological and public health effects and has come under increased scrutiny by both environmental scientists and regulatory agencies. For many regions though, including the Sahel of Tunisia, little is known about the NO_3^- sorption capacity of soils. In this project we measured NO_3^- sorption by a profile of an *iso-humic* soil from Chott Meriem, Tunisia. Soil samples were collected from four soil depths (0–25, 25–60, 60–90, and 90–120 cm) on 1 June 2011, and their sorption capacity was determined using batch experiments under laboratory conditions. The effects of contact time, the initial concentration, and the soil-solution ratio on NO_3^- sorption were investigated. In general, the results suggested that NO_3^- was weakly retained by the Chott Meriem soil profile. The quantity of NO_3^- sorption increased with depth, contact time, initial concentration, and soil-solution ratios. To evaluate the sorption capacities of the soil samples at concentrations ranging between 25 and 150 mg L^{-1} experimental data were fitted to both Freundlich and Langmuir isotherm sorption models. The results indicated that Freundlich model was better for describing NO_3^- sorption in this soil profile.

1. Introduction

Nitrogen (N) is a critical nutrient needed by all plants for growth [1]. Input of inorganic N as a fertilizer is considered essential in modern agriculture in order to satisfy the dietary needs of a growing world population. Nitrate (NO_3^-) is the one of the principal N forms taken up by plants. As such, inorganic N is widely used in agriculture and numerous studies have suggested that leaching of NO_3^- following high input rates of chemical fertilizer and due to mineralization of organic N already present in the soils can cause degradation of surface and groundwater quality. Excess NO_3^- contaminated water supplies have been linked to outbreaks of infectious disease [2]. Also, NO_3^- can be converted to nitrite in the digestive tracts of infants and ruminant animals, which then combines with blood hemoglobin, reducing its ability to carry oxygen, occasionally leading to death. The ability of soil to adsorb anions can reduce NO_3^- leaching to the deeper horizons and maximize the NO_3^- available for plant nutrition and can thus play a fundamental role in enhancing soil nutrition in regions, such as Mediterranean areas, where NO_3^- availability is often a limiting factor [3]. Previous studies have reported the sorption of NO_3^- by soils [4, 5]. However, NO_3^- mobility in soils is mainly controlled by a number of soil properties including iron and aluminum oxide concentrations [6], organic matter content [7], pH of soil solutions [8], and soil texture and clay mineralogy [9]. Other studies suggested that sorption of NO_3^- was influenced by the competition with other anions as Cl$^-$ [10]. Qafoku et al. [11] reported that NO_3^- sorption was directly related to NO_3^- concentration in the soil solution.

The NO_3^- sorption process has been studied in many different soil orders in tropical latitudes [12], including Oxisols [13] as well as in ultisols of the southeastern and mid-Atlantic United States [14] and in forest soils of the American northwest [15]. However, none of these investigated NO_3^- dynamics for the soils of Tunisia, in particular the soils of the Sousse region, which is considered to be one of the most important crop production areas in Tunisia. The aim of this

TABLE 1: Physiochemical properties of *iso-humic* soil from Chott Mariam.

	Depths			
	0–25 cm	25–60 cm	60–90 cm	90–120 cm
pH	8.12	8.41	8.56	8.54
CEC (meq/100 g of soil)	19.72	22.04	23.45	23.45
OM (%)	0.7	0.9	1.1	1.3
Total C ($mg\,kg^{-1}$)	10988	8255	20988	27093
Total N ($mg\,kg^{-1}$)	900	540	510	260
N-NO_3 ($mg\,kg^{-1}$)	86.47	36.15	169.25	38.21
N-NH_4 ($mg\,kg^{-1}$)	6.68	3.29	3.57	3.39
Exchangeable P ($mg\,kg^{-1}$)	93.68	20.9	4.12	4.99
Exchangeable Na ($mg\,kg^{-1}$)	57.5	232.3	533.6	124.2
Exchangeable Al ($mg\,kg^{-1}$)	76.68	87.23	72.79	51.55
Exchangeable Ca ($mg\,kg^{-1}$)	5450.38	5508.61	5874.56	17306.04
Exchangeable K ($mg\,kg^{-1}$)	491.23	299.77	135.49	106.61
Exchangeable Mg ($mg\,kg^{-1}$)	410.16	433.23	356.83	461.68
Exchangeable Mn ($mg\,kg^{-1}$)	59.16	52.54	22.95	4.22
Exchangeable Fe ($mg\,kg^{-1}$)	33.57	24.62	9.01	3.38
Clay (%)	12.8	24.4	30.5	25.8
Silt (%)	38	15.2	10	15.2
Sand (%)	49.2	60.4	59.5	59.1
Texture	Sandy loam	Sandy loam	Clay	Clay loam

study was to investigate the NO_3^- sorption capacity of these soils by soil depth.

2. Materials and Methods

2.1. Site Description. Soil samples were collected from a citrus orchard at the High Agronomic Institute of Chott Meriem Sousse, ($35°54'N10°36'E$) on 1 June 2011. The climate is Mediterranean and is characterized by hot dry summers and moderate wet winters, an average annual precipitation of 230 mm and a mean annual temperature of 18.5°C. Ammonium nitrate fertilizer is applied annually at a rate of 200 kg N ha^{-1}. The soils are medium-textured brown *iso-humic* [16], with an average infiltration rate of 45 mm h^{-1}.

2.2. Chemical Analysis. Four soil pits were sampled to a depth of 120 cm and separated into four depths: 0–25, 25–60, 60–90, and 90–120 cm. Samples were air-dried and ground to pass a 2 mm sieve. Soil pH was determined in 1 : 2 soil : water suspension [17]; organic matter (OM) determined by the wet oxidation method (Walkley and Black); particle-size distribution by the pipette method [18]; cation exchange capacity (CEC) by the BaCl$_2$ extraction method [19]. Mehlich-III [20], P, Ca, Mg, Fe, Al, Cd, Cu, and Mn were determined by equilibrating 2.5 g of air-dried soil sample with 25 mL of Mehlich-III extracting solution for 5 min and filtering through Whatman no. 40 filter paper. The different concentrations in the extracts were measured using an inductively coupled plasma optical emission spectrometer (Perkins Elmer, Model 4300DV). Soil N-NO_3^- and N-NH_4^+ concentrations were analysed using the steam distillation method [21].

2.3. Batch Study. The NO_3^- sorption on the *iso-humic* soil of Chott Meriem was studied as a function of the soil to soil-solution NO_3^- ratio. Nitrate sorption in each horizon was determined via batch equilibration techniques adapted from [14]. The following soil: solution ratios (1%, 12.5%, 25%, and 50%) have been proposed in the literature [22] and were used in this study. The concentration of the solution was 100 mg NO_3^- L^{-1}. The temperature was 20°C. Briefly 5 g of air-dried soil from each soil subsample was equilibrated with 100 mL of NO_3^- solution. Two drops of toluene were added to each mixture to prevent any biological NO_3^- transformations. Equilibration was estimated to have occurred after the mixture was shaken on a reciprocal shaker at 20°C for 1 h at a rate of 100 oscillations/min. After equilibration the mixtures were centrifuged at 5000 rpm for 10 min and the NO_3^- concentration of the supernatant was determined immediately using a spectrophotometer at 220 nm.

The amount of adsorption at equilibrium Q_e (mg g^{-1}) was calculated by

$$Q_e = \left(\frac{C_i - C_e}{M} \right) \times V, \tag{1}$$

where C_i and C_e (mg L^{-1}) are the liquid-phase concentrations of NO_3^- at initial conditions and at equilibrium, respectively. V is the volume of the solution (L). M is the mass of dry adsorbent used (g).

3. Results and Discussion

3.1. Soil Properties. The main soil properties thought to influence NO_3^- sorption and movement are provided in Table 1.

The pH for these soil horizons were all above 8, while soil texture varied between fine sandy loam and sandy clay loam in the two first horizons (0–25 cm) and (25–60 cm) and clay and sandy clay loam, for the two next deeper horizons (60–90 cm and 90–120 cm), respectively. The variation in texture reflected the differences in parent materials [23]. Clay content, which tended to increase with depth, can affect soil fertility and water and nutrient holding capacities as well as plant root movement [24]. The organic matter content for the different soils horizons showed a similar pattern to the clay, where the concentrations tended to increase in the deeper horizons (Table 1). It has been reported that NO_3^- mobility is often related to the organic matter content and could be due to the higher cation exchange capacity [25]. The amount of exchangeable cations differed markedly; Ca^{2+} concentrations were high in the different horizons and tended to increase at depth. The inverse can be seen for other exchangeable cations such K^+ and Fe^{2+} 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.

3.2. Effect of Contact Time on NO_3^- Sorption. As shown in Figure 1, the NO_3^- adsorption rate was rapid for the first 60 min and decreased over time. Equilibrium sorption was established after approximately 120 min for NO_3^- ions at an initial concentration of 100 mg L^{-1}. From the results it can be seen that the contact time required for maximum sorption of NO_3^- by different soil profile was dependent on the initial NO_3^- concentration and on certain soil components, especially the OM and clay content. This behavior suggests that at the initial stage, sorption takes place rapidly on the external surface of the adsorbent followed by a slower internal diffusion process, which may be the rate-determining step. This trend in NO_3^- sorption suggests that the binding may be through interactions with functional groups located on the surface of the soil. According to these results, the contact time was fixed at 120 min for the batch experiments to make sure that equilibrium was attained. The results demonstrated that at a fixed adsorbent dosage, the NO_3^- sorption was higher in deeper horizons than in superficial horizons. The two deepest horizons contained more organic matter, which counterbalances the effect of positive charges of the oxides on NO_3^- sorption. Indeed, organic groups displace water ligands at the positively charged sites on surfaces oxides [26]. As shown in Table 1 the amount of clay increased with depth along with increasing CEC, which enhances the NO_3^- sorption capacity.

3.3. Effect of Soil-Solution Ratios on NO_3^- Sorption. The sorption of NO_3^- on *iso-humic* soil of Chott Meriam was studied as a function of the soil to soil-solution NO_3^- ratio. The following soil : solution ratios (1%, 12.5%, 25%, and 50%) have been proposed in the literature [22] and used in this study. The experiment was conducted in batch. As shown in Figure 2 there was not a lot of variation between the different depths in the NO_3^- adsorption capacity at a low soil : solution ratio (1%). However, the NO_3^- sorption capacity increased with an increase in the soil : solution ratio. When the ratio increased
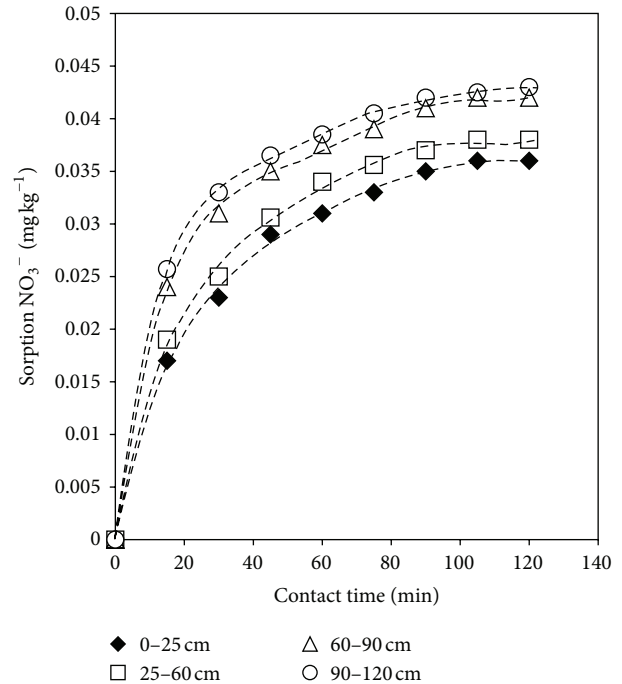

FIGURE 1: Effect of contact time on NO_3^- sorption for 4 soil depths from a batch experiment using an *iso-humic* soil from Chott Meriam, Tunisia. (Initial conditions for the batch experiment were 100 mg NO_3^- L^{-1}, 22°C, and 5 g air-dried soil).
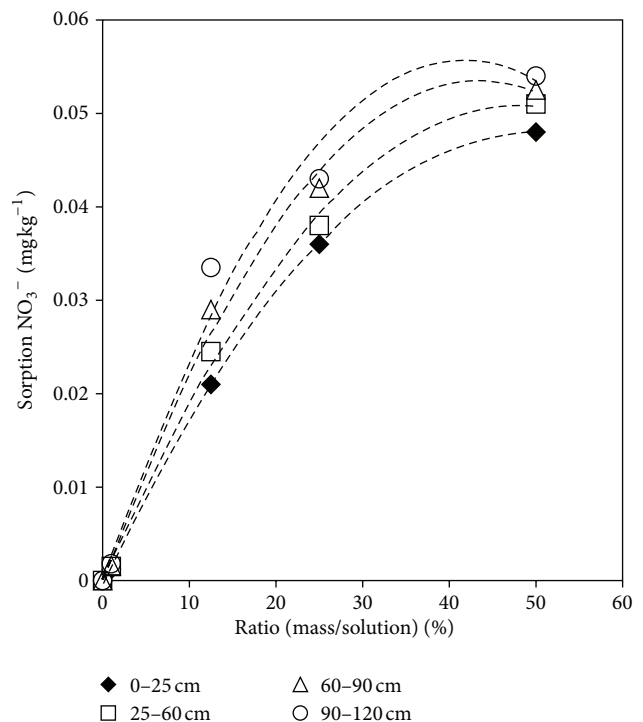

FIGURE 2: Effect of soil-solution ratios on NO_3^- sorption for 4 soil depths from a batch experiment using an *iso-humic* soil from Chott Meriam, Tunisia (soil/solution ratios: 1%, 12.5%, 25%, and 50%, 22°C, 24 h).
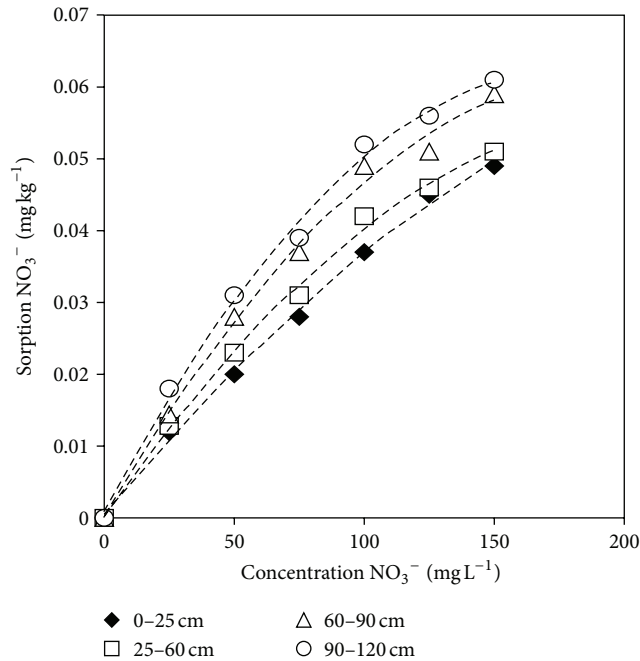
FIGURE 3: Effect of initial NO_3^- concentration on NO_3^- sorption for 4 soil depths from a batch experiment using an *iso-humic* soil from Chott Meriam, Tunisia (25, 50, 75, 100, 125, and 150 mg L^{-1}, 22°C, 24 h, and soil mass = 5 g).

TABLE 2: Langmuir and Freundlich parameters for sorption of NO_3^- on four depths of *iso-humic* soil from Chott Mariam, Tunisia.

		Depths			
		0–25 cm	25–60 cm	60–90 cm	90–120 cm
Langmuir parameters	Q (mg/g)	0.153	0.134	0.144	0.121
	K_L (L/mg)	0.0031	0.0041	0.0046	0.0068
	R^2	0.89	0.95	0.93	0.97
Freundlich parameters	K_F	0.00086	0.001	0.0012	0.002
	n	1.23	1.27	1.28	1.44
	R^2	0.99	0.99	0.98	0.99

from 1% to 50%, the NO_3^- sorption capacities increased from 0.0012 to 0.048, 0.0015 to 0.051, 0.0016 to 0.0525, and 0.0018 to 0.054 for the 0–25, 25–60, 60–90, and 90–120 cm depths, respectively. These observations infer that increasing soil : solution ratios play a major role in the increasing NO_3^- sorption capacity by the soils, similar to results obtained by Qafoku et al. [11]. It can be noted that the ratio increases as the mass of soil increases. It has been suggested that increased soil mass causes increased variable charges in the solution and consequently increased sorption of NO_3^-. Furthermore, it was reported that NO_3^- mobility was often related to the active components of organic matter and the clay-sized fractions [27], likely due to the resulting increase in CEC [25].

3.4. Effect of Initial NO_3^- Concentration on NO_3^- Sorption. Seeing that the initial NO_3^- concentration in solution provides an important driving force to overcome mass transfer limitations of NO_3^- between aqueous and solid phases, a higher initial NO_3^- concentration will increase the sorption process. The effect of initial NO_3^- concentration on NO_3^- sorption for all soil depths was investigated in the

following concentrations (25, 50, 75, 100, 125, and 150 mg NO_3^- L^{-1}). Figure 3 shows the change of the equilibrium sorption capacity of soil samples with different initial NO_3^- concentrations. It was observed that the amount of sorbed NO_3^- at equilibrium increased with increasing initial NO_3^- concentration for all soil horizons, although rates differed according to the soil layer.

Many previous works reported that at low concentration, more NO_3^- is sorbed by the soil than is left in solution. There is some controversy concerning the mechanism of NO_3^- adsorption at low concentration in soil. Toner et al. [28] proposed a totally reversible adsorption, which is a simple electrostatic retention (i.e., the adsorption is the result of van der Waals type interactions). On the contrary, Qafoku et al. [11] explained the adsorption as an overlapping or interpenetration of double layers around positively charged Al-polymers and negatively charged silicate minerals.

Below concentrations of 100 mg NO_3^- L^{-1}, NO_3^- sorption was low in the top horizon (0–25 cm), higher in the 25–60 cm horizon, and peaked within the 60–90 cm and 90–120 cm depths. Above concentrations of 125 NO_3^- mg L^{-1},

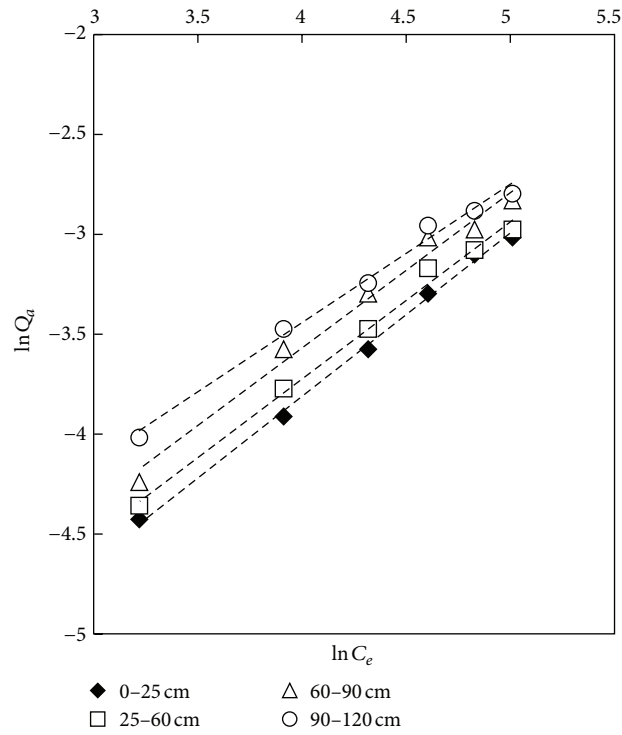FIGURE 4: Langmuir isotherms for NO_3^- sorption by soil profile at (25, 50, 75, 100, 125, and 150 mg NO_3^- L^{-1}, 22°C, 24 h, and soil mass = 5 g).
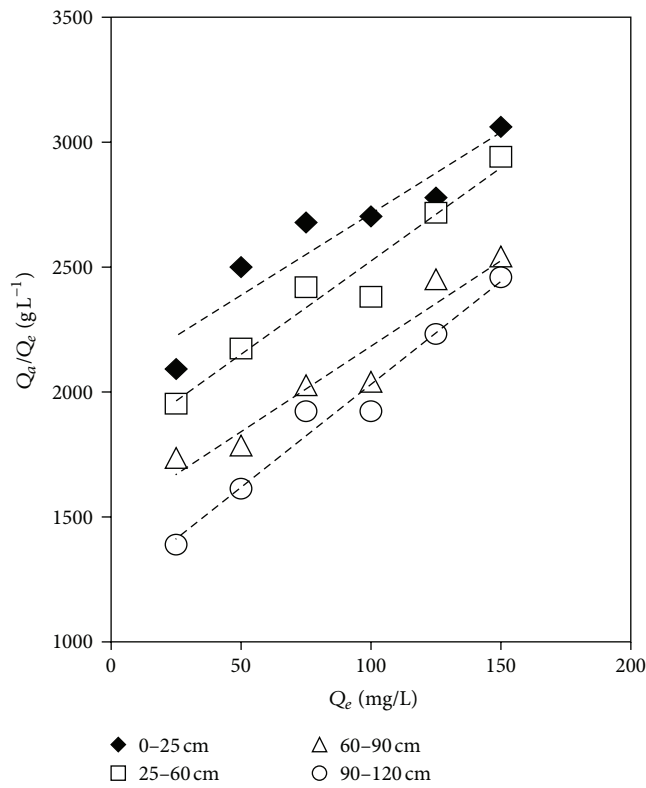

FIGURE 5: Freundlich isotherms for NO_3^- sorption by soil profile at (25, 50, 75, 100, 125, and 150 mg NO_3^- L^{-1}, 22°C, 24 h, and soil mass = 5 g).

the slope of the curves decreased. This decline in NO_3^- sorption with increased initial concentrations in all soil depths is likely due to the weakening of attractive forces between NO_3^- and the soil matrix as well as desorption of other anions (e.g., P) as suggested by Strahm and Harrison [15].

3.5. Adsorption Equilibrium and Isotherms. To facilitate the estimation of the NO_3^- sorption capacities of the soils at the following concentrations (25, 50, 75, 100, 125, and 150 mg NO_3^- L^{-1}), the experimental data were fitted to the Freundlich and Langmuir equilibrium adsorption isotherm models. The Langmuir equation is as follows: $C_e/Q_e = 1/Q_m b + C_e/Q_m$, where C_e is the equilibrium concentration of NO_3^- in the solution (mg/L), Q_e the amount of NO_3^- sorbed per unit weight of soil (mg kg^{-1}), and Q_m and b are the Langmiur constants signifying the sorption capacity of the adsorbent and energy of the sorption process, respectively. The sorption data was plotted (Figure 4), and Q_m and K_L (listed in Table 2) were calculated from the intercept and the slope of the plots.

The Langmuir equation characterized the NO_3^- sorption data fairly well, with R^2 values between 0.89 and 0.97 for the different soil horizons (Table 2). The adjusted R^2 values suggest that the Langmuir isotherm provides a good model of the sorption system only for the 25–60 cm and 90–120 cm horizons. In this work, it appears that the Q_m was greatest in the surface horizon and tended to decrease with depth. However, K_L increased with depth, which suggests that not all inorganic sites may be available for NO_3^- binding [15].

The Freundlich equation is as follows: $\ln(q_e) = \ln(K_F) + (1/n)\ln(C_e)$, where q_e is the amount of NO_3^- per gram of soil at the equilibrium, C is the NO_3^- concentration in solution at the equilibrium, and K and n are the empirical constants indicating the adsorption capacity and adsorption intensity, respectively. Figure 5 shows the plot of $\ln(q_e)$ versus $\ln(C_e)$, enabling the constants K and n to be determined from the intercept and slope, respectively (Table 2). The R^2 values for the Freundlich isotherm model were greater than those from the Langmuir model (Table 2). The values of n for all soil samples were found to be nearly similar at all depths, indicating reasonable sorption of NO_3^- onto soil samples at the concentration studied, as is evident from Table 2. Additionally it can be also shown that the values of (K_F), which is a measure of the degree of sorption, decrease at greater depths, consistent with previous studies [15].
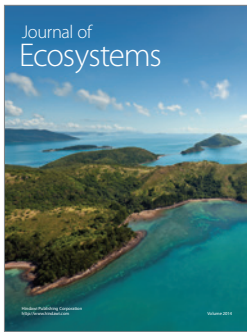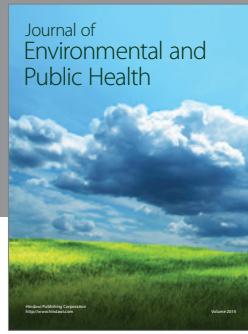
4. Conclusion

In this study, the sorption of NO_3^- from aqueous solutions onto alkaline soils of the Chott Meriem region was examined. The results indicated that the soil NO_3^- sorption capacity of different horizons was affected by the ratio of the soil mass and solution volume, the initial NO_3^- concentration, and the contact time. The amount of NO_3^- sorbed on soils increased with depth. However, a considerable amount of NO_3^- in the soil was not sorbed by the soil and, thus, it is expected that the majority of NO_3^- in excess of biological immobilization rates will be transported through the soils into ground or surface waters. Also, although both Langmuir and Freundlich isotherm models were used to describe the sorption behavior of NO_3^- on soil samples, the Freundlich adsorption isotherm model better described the NO_3^- sorption in this soil profile.

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