



Desorption of Adsorbed Ammonium in Some Gypsiferous Soils, Tikrit Governorate, Iraq

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ABSTRACT

This study aimed to investigate the ability of Gypsiferous soil to desorb the adsorbed ammonium in Gypsiferous soils. Desorption of ammonium by Gypsiferous soils is a significant process to identify the rout of ammonium nitrogen in soil systems. Two samples of Gypsiferous soils were collected from Tikrit University and Al-Alam city fields. The samples were contained different gypsum concentrations: low 65 g kg⁻¹ and high 235 g kg⁻¹. Soil columns were utilized by using the method of (Head Constant) and various concentrations of ammonium (5, 10, 20, 40, 80, 100, 120 and 150) mg_(NH₄) L⁻¹ was added. Then, samples were collected at different times (1, 2, 4, 8, 24, and 48) hr; then, 0.01 M of KCl were added to each of the soil columns in order to desorb the adsorbed ammonium in the first stage. Best fitting of different kinetic models have been used to evaluate the desorption process (Zero order, First order, Diffusion, Power function, and Elovich models). The ammonium desorption in Gypsiferous soils was found to conform to the Power function equation more than the other used equations. The results showed that the process of ammonium desorption was affected by the content of calcium carbonate in soil.

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Keywords: Desorption, Ammonium, Gypsiferous soil, Power function equation.

1. Introduction

Soil is considered a non-renewable source for agriculture, and it is essential for providing the basis for food production. Gypsiferous soil is a type of soil that is characterized by a low to high concentration of di-hydrated calcium sulphate, which may range between 5 to more than 95%^[1]. This type of soil is found in arid and semi-arid areas, and is poor in organic matter content^[2]. These soils are vulnerable to degradation, especially in overuse cases; however, they can be productive with appropriate practices of management^[3,4]. High contents of gypsum in soil may lead to a decrease in the amount of available water and ultimately affect soil structure^[5,6].

Ammonium is considered as the major form of nitrogen fertilizer that is applied in agricultural processes. For plant growth, ammonium in soil is not only a major source of nitrogen, but also as it is significant in the processes of nitrogen transformation^[7-9]. Among various sources of available Nitrogen, most studies have focused on ammonium, because it is present in cropland and natural soils at higher levels^[10]. Ammonium has harmful effects on plant growth in excessive quantities^[11].

However, ammonium may present in small quantities in soil solutions, as it is more prone to transformation than nitrate^[12]. Mostly, the plants benefit from nitrate and ammonium in the soil to increase their contents of nitrogen^[13]. Ammonium is usually adsorbed by clay minerals and organic matter, while it escapes with irrigation water^[14]. Therefore, ammonium transport is strongly dependent on oxidation conditions^[15]. The desorption of ammonium in the soil is influenced by several factors, including soil structure, texture, temperature, moisture content, calcium carbonate, gypsum content and some other elements^[16]. Therefore, the process of ammonium desorption in different types of soils may present great variability. No studies examined the desorption of adsorbed ammonium in gypsum soils were found by the authors. This experiment aims to study the kinetics of ammonium desorption by examining the best kinetic equation that describes the ammonium's desorption.

2. Materials and Methods

2.1 Sample collections and analysis

Sampling stations have been selected based on the contents of gypsum in soil, which include low content of gypsum (L1) 65 g kg⁻¹ and high content of gypsum (L2) 235 g kg⁻¹^[17,18]. The samples were collected from two fields in the University of Tikrit and Al-Alam City, and the samples were taken for a depth of 0-

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30 cm. The samples were submitted to chemical and physical analyses; the characteristics of the soil samples are shown in Table 1.

Table 1: Physicochemical characteristics of the experimental soils.

Soil Characteristics	Unit	Samples	
		Location 1	Location 2
pH		7.5	7.69
EC	dS m ⁻¹	2.52	2.31
CaSO ₄ .2H ₂ O	g kg ⁻¹	65	235
CaCO ₃		230	110
O.M		9	8
CEC	Cmol kg ⁻¹	13.39	10.9
Sand	g kg ⁻¹	669	745
Silt		77	52
Clay		255	211
Texture		S.C.L	S.C.L
N	mg kg ⁻¹	18.5	12.7
P		5.5	1.5
K ⁺		112.8	64.89
Na ⁺	mmol L ⁻¹	1.30	2.32
K ⁺		0.88	0.59
Ca ²⁺		5.61	13.41
Mg ²⁺		6.43	3.23
Cl ⁻		2.84	1.73
CO ₃		Nil	Nil
HCO ₃		1.33	2.31
SO ₄ ⁼		9.87	15.43

2.2 Ammonium adsorption and desorption

Soil columns with (0.25) m length and a (0.065) m in diameter were utilized by using the method of (Head Constant); then, various concentrations of ammonium (5, 10, 20, 40, 80, 100, 120 and 150) mg_(NH₄)L⁻¹ was added. Also, times of the first drop for each column were recorded immediately; then, samples were collected after the following periods (1, 2, 4, 8, 24, and 48) hr. In

order to desorb the adsorbed ammonium in the first stage, 0.01 M of KCl was added to each soil column.

The equations are applied in this research are: zero order, first order, diffusion, power function, and Elovich. The mathematical formulas of these equations are the numbered equations from 1 to 5, respectively, as shown in the following^[19]:

Zero order equation:

$qt = q_0 - kt$ 1

First-order equation:

$\ln \ln qt = \ln \ln q_0 - kt$ 2

Parabolic diffusion equation:

$qt = q_0 - k\sqrt{t}$ 3

Power function equation:

$\ln \ln qt = \ln \ln q_0 - k \ln \ln t$ 4

Elovich equation:

$qt = q_0 - k \ln \ln t$ 5

Where:

qt is the measured concentration at the time (t)

q₀ represents the concentration at the time of (zero)

K is constant.

The amounts of adsorbed and desorbed NH₄ were calculated based on the following equation:

$q = (C_0 - Ct). V/m$ 6

The REM program was utilized in order to determine the best equation that describes ammonium desorption or adsorption you concentrate in your study on desorption; also, some other values were used, including: the lowest value of the standard error (SE) and the highest value of the correlation coefficient^[20].

3. Results and discussion

3.1 Desorption of adsorbed ammonium

Tables 2 and 3 show an increase in the amount of desorbed ammonium with an increase in the initial concentration of the added ammonium and with an increase in the period in both samples. Regarding low gypsum content soil, the maximum desorbed was 3.92 mg kg⁻¹ for the concentration of 150 mg L⁻¹ for a period of 48 hours. As for the lowest desorbed, it reached 0.84 mg kg⁻¹ for the concentration of 5 mg L⁻¹ over a period of 1 hour.

Table 2: Amounts of desorbed ammonium in soil with a low gypsum content.

Added amount of (NH ₄) mg L ⁻¹								Time (h)
150	120	100	80	40	20	10	5	
Desorbed amount of (NH ₄)								
2.24	1.96	1.68	1.68	1.4	1.26	1.12	0.84	1
2.66	2.1	1.96	1.4	1.68	1.4	1.4	1.12	2
2.8	1.68	2.1	1.82	1.96	1.54	1.4	1.4	4
3.08	2.38	2.38	2.1	2.24	1.68	1.68	1.4	8
3.5	2.8	2.66	2.1	2.38	1.4	1.96	1.82	24
3.92	3.5	3.08	2.8	2.66	2.8	2.24	2.1	48
3.03	2.4	2.31	1.98	2.05	1.68	1.64	1.45	Mean

For the low gypsum content soil, the maximum desorbed of ammonium was 3.92 mg kg⁻¹ for the concentration of 150 mg L⁻¹ over a period of 48 hours. Otherwise, the lowest ammonium

desorbed, reached 0.56 mg kg⁻¹ for the concentration of 5 mg kg⁻¹ for a period of 1 hour. Overall, the desorbed ammonium in soil with low gypsum was higher than that of high gypsum content.

Table 3: Amounts of desorbed ammonium in soil with a high gypsum content.

Added amount of (NH ₄) mg L ⁻¹								Time (h)
150	120	100	80	40	20	10	5	
Desorbed amount of (NH ₄)								
1.4	1.26	1.26	1.12	1.12	0.84	0.7	0.56	1
1.68	1.68	1.4	1.26	1.4	1.12	0.98	0.7	2
1.96	1.96	1.4	1.54	1.96	1.4	1.26	1.12	4
2.8	2.66	1.82	1.96	2.38	1.82	1.4	1.4	8
3.36	3.08	2.52	2.52	2.66	2.1	2.1	1.68	24
3.92	3.36	3.22	2.94	2.8	2.8	2.52	1.82	48
2.52	2.34	1.94	1.89	2.05	1.68	1.49	1.21	Mean

It is believed that the amounts of adsorbed and desorbed ammonium are proportional to the amounts of (CaCO₃) in the soil^[21,22]. Also, most of the displaced ammonium is ammonium adsorbed on non-specialized sites^[23]. Therefore, the desorbed ammonium in the soil of the study area was affected by the presence of calcium carbonate, which means that the adsorbed ammonium was subjected to precipitation processes on the solid phase that affected its released quantities.

3.2 The Kinetic approach of NH₄ desorption

The standard coefficient of determination (R²) and standard error (SE) values were used to determine the best equations for

describing ammonium desorption in the studied soil samples. The tables 4 and 5 represent summarize of the results of the statistical analysis using the five equations for the soils with low and high gypsum-content.

The results indicate that the values of R² for the power function equation are 0.95, 0.97, 0.55, 0.94, 0.78, 0.98, 0.73, and 0.98, respectively. While the value of the standard error (SE) are 4.03, 2.93, 2.3, 2.59, 2.23, 2.28, 2.24, and 1.95 for the added amounts 5, 10, 20, 40, 80, 100, 120, and 150 mg L⁻¹, respectively.

Table 4: R2 and SE values of Ammonium desorption in low gypsum content soil.

L1 Conc. mg L ⁻¹	Equations									
	Zero order		First order		Diffusion		Power function		Elovich	
	R ²	SE	R ²	SE	R ²	SE	R ²	SE	R ²	SE
5	0.832	0.170	0.717	1.479	0.929	3.588	0.95	4.03	0.973	6.146
10	0.867	0.137	0.792	1.299	0.955	3.276	0.97	2.93	0.973	5.531
20	0.756	0.255	0.723	1.366	0.66	3.714	0.55	2.30	0.534	5.574
40	0.728	0.221	0.649	1.519	0.861	3.53	0.94	2.59	0.972	6.275
80	0.847	0.171	0.779	1.478	0.856	3.602	0.78	2.23	0.788	5.772
100	0.875	0.715	0.809	1.701	0.96	4.038	0.98	2.28	0.983	6.835
120	0.91	0.180	0.841	1.759	0.893	5.042	0.73	2.24	0.762	7.769
150	0.856	0.209	0.790	2.172	0.95	4.8	0.98	1.95	0.986	8.179
Average	0.834	0.257	0.763	1.597	0.883	3.9489	0.86	2.57	0.8719	6.5105

The results indicate that the values of R² for the power function equation are 0.92, 0.98, 0.97, 0.9, 0.99, 0.94, 0.95, and 0.97, respectively. While the value of the standard error (SE) are 6.18, 6.1, 5.46, 4.27, 4.64, 4.27, 4.35, and 4.6 for the added levels (5, 10, 20, 40, 80, 100, 120 and 150 mg L⁻¹, respectively).

Statistical analysis for best fitting of models indicates that all models can describes the ammonium desorption at different

degrees depending on R2 and SE. The success of different models can be arranged as the following:

Power function > Elovich > Diffusion > Zero order > First order

According to the (R²) and (SE) values, the results also indicate that the best model that describe ammonium desorption in soil with low and high gypsum content is the (Power function equation).

Table 5: R2 and SE values of Ammonium desorption in high gypsum-content soil.

L2 Conc. mg L ⁻¹	Equation									
	Zero order		First order		Diffusion		Power function		Elovich	
	R ²	SE	R ²	SE	R ²	SE	R ²	SE	R ²	SE
5	0.703	0.255	0.586	1.247	0.853	3.882	0.92	6.18	0.971	6.925
10	0.898	0.200	0.772	1.336	0.978	5.545	0.98	6.10	0.978	9.269
20	0.882	0.223	0.752	1.409	0.957	5.675	0.97	5.46	0.970	9.560
40	0.637	0.375	0.551	1.597	0.8	5.012	0.90	4.27	0.949	9.132
80	0.880	0.228	0.794	1.500	0.973	5.805	0.99	4.64	0.983	9.759

100	0.968	0.125	0.918	1.526	0.991	6.285	0.94	4.27	0.904	10.03
120	0.842	0.383	0.646	1.789	0.883	6.366	0.95	4.35	0.981	11.219
150	0.836	0.369	0.742	1.950	0.944	7.927	0.97	4.60	0.98	13.505
Average	0.831	0.270	0.720	1.544	0.922	5.812	0.95	4.98	0.964	9.925

3.3 Desorption velocity coefficient

Table 6 shows that the values of the ammonium desorption velocity coefficient of the Power function equation in the low gypsum soil content ranged between 0.892 and 0.798 mg kg day⁻¹ for the treatments 150 and 5 mg L⁻¹, respectively.

Table 6: Ammonium desorption rate coefficient values in the studied soils based on the Power function equation (mg kg hr⁻¹) and soil hysteries values.

Treatments mg L ⁻¹	Low gypsum soil	Soil hysteries values	High gypsum Soils	Soil hysteries values
5	0.798	2.2	0.775	1.27
10	0.881	8.47	0.839	15.83
20	0.869	32.92	0.909	50.17
40	0.854	80.78	0.918	117.17
80	0.890	181.54	0.885	264.03
100	0.863	266.44	0.889	328.69
120	0.883	277.98	0.894	390.51
150	0.892	350	0.877	500.51
Ave.	0.867	150.04	0.873	208.52

However, the values of the desorption velocity coefficient of the Power function equation in the high gypsum soil content range between 0.877 and 0.775 mg kg day⁻¹ for the treatments 150 and 5 mg L⁻¹, respectively. Also, the soil hysteries values of high gypsum soils were higher than low gypsum soils as the phenomenon of soil hysteria is the discrepancy between the adsorbed and the desorbed amount of ammonium.

Since the Power function equation is exponential; so, the process of desorption begins quickly on the adsorption surfaces then most of the ammonium desorbed in high concentrations is associated with the specific and nonspecific adsorption surfaces. Regarding the desorption of ammonium at low concentrations, it may occur on nonspecific adsorption surfaces^[24,25]. The ammonium adsorption process in the soil of the study area was influenced by the presence of calcium carbonate, which means that the adsorbed ammonium was subjected to precipitation processes on the solid phase that affected its desorbed quantities.

Conclusion

This study aims to investigate the kinetics of ammonium desorption by examining the best kinetic equation that describes the ammonium's desorption. Also, best fitting of different kinetic models was used to evaluate the desorption process (Zero order, First order, Diffusion, Power function, and Elovich models). The Power function equation has successfully described the ammonium desorption kinetics in different types of Gypsiferous soil, including low content 65 g kg⁻¹ and high content 235 g kg⁻¹. This study concluded that the ammonium desorption process is not affected by the content of gypsum, while it has been affected by the presence of calcium carbonate, which means that the

adsorbed ammonium was subjected to precipitation processes on the solid phase, which affect its released quantities.

Conflict of interests

None

Author Contribution

Muhammed Obaid Muhammed: Conceive the idea, data collection and write-up of the paper. Basim Shakir Al-Obaidi: Revise the manuscript, discuss the results and data analysis as well as supervised the work.

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