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Study of magnesium status and its reactions in some calcareous soils.

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Abstract

A laboratory experiment was conducted with the aim of studying the adsorption of magnesium from the compound hydrated magnesium sulphate (MgSO4.7H2O) and its relationship to some soil properties in five calcareous soils from central Iraq. Three physicochemical equations were used (Langmuir and Freundlich and Temkin) to describe Mg adsorption. The simple correlation coefficient (r), coefficient of determination (r2) and the best equation was chosen according to highest value of r, r2 and t and least value of Standard error of estimate (SE.e(. The results showed the superiority of the Freundlich and Langmuir equations in describing and evaluating magnesium adsorption compared to the Temkin equation. Freunglich equation was more efficient for describing Mg adsorption compared with other physicochemical equations used, depending on highest values of correlation coefficient (0.982), coefficient of determination (0.964), t value (23.115), and the lowest standard error (0.080), then followed by the Langmuir equation, its statistical indicators reached 0.980, 0.957, 12.921, and 0.179 for the correlation coefficient, coefficient of determination, t value, and minimum standard error of estimate, respectively. The efficiencies were 98.0, 95.7, and 78.1% for the Freundlich, Langmuir, and Temkin equations, respectively. Maximum adsorption capacity in study soils were 350.0, 950.0, 620.0, 880.0, 450.0 mg Mg kg-1soil while the binding strength were 0.047, 0.005, 0.003, 0.003 and 0.084 ml Mg mg-1 for Al-Jadriya, Baqubah, Al-Youssoufia, Karma, and Wasit soils respectively. The amount of magnesium adsorption as a mean of study soil reached to 32.3% of the added Mg, and 67.7% of it remained dissolved in the soil solution. Freunglich adsorption constants (lnKf and 1/n) significantly correlated with Langmuir maximum adsorption (b) and binding strength (K). Also, the maximum adsorptive capacity (b) of Langmuir equation statistically related to soil properties (CEC, Organic matter content OM, total and active carbonate minerals and plant available Mg.It is concluded that the Freundlich and Langmuir equations were more suitable for describing Mg adsorption in study soils. Soil Mg adsorption was according to the following arrangement: Baqubah > Al-Karma > Al-Youssoufia > Wasit > Al-Jadriyah.

Key words: Freundlich , Langmuir, Maximum adsorption, Binging strength.

Introduction

Magnesium is one of the most important basic nutrients in plant nutrition due to its effective role in many vital processes in the plant, such as the process of photosynthesis, as it is included in the chlorophyll molecule, and magnesium is the mineral key to it, as each chlorophyll molecule contains one atom of magnesium, which constitutes approximately 2.7% of the chlorophyll molecule. The chlorophyll molecule represents 15-30% of the total magnesium in the plant. Most magnesium is found in chloroplast [1]. Magnesium also has a role in activating all the enzymes responsible for the process of photophosphorylation, as it forms a bridge between the phosphates that return to ATP and ADP and the enzyme molecule. Magnesium is also necessary for the activity of key enzymes such as: phosphoenol pyruvate carboxylase and Ribulose 1-5 Bisphosphate Carboxylase [2 and 3]. It has been found that its content in most crops ranges between 0.1 - 1% on a dry weight basis, and this depends on the plant characteristics (type and class of plant, plant family, plant density, growth stage, and root system) and soil characteristics (soil texture, content and type of clay minerals, CEC, aeration, and carbonate minerals). and on climate and environment (temperature, humidity, and precipitation) [4, 5 and 6] . The results of many studies have shown that most economic plants, especially grain and vegetable crops growing in different soil systems and to a large extent in calcareous soils, respond to fertilization with magnesium added to the soil or to foliar feeding [7, 8, and 9]. Magnesium constitutes 1.93% of the composition of the Earth's crust [10 and 2].

Material and Methods

Mg is a common constituent in many minerals, comprising 2% of earth's crust, the amount of Mg released from soil minerals is generally small compared with the amount needed to high crop yield and quality [11]. It has been found that the magnesium content in most agricultural soils ranges from 0.6 to 6.0, with a general average of 5.0 g kg-1 soil [10]. Magnesium availability is affected by several factors, including soil texture, clay content and type, organic matter content, degree of soil interaction, and magnesium concentration in the soil solution [12, 13, 11, 14 and 15].

Generally, the availability of applied fertilizer in soil solution is controlled by adsorption -desorption process and its partition between the solution and the solid phases [16 and 17]. In the available publications where the application of magnesium fertilizer (dolomite) have been recommended, the various authors made their recommendation based on agronomic soil test without considering the portion of fertilizer that might be adsorbed within the soil system. As recovery of ionic nutrients in applied fertilizer is typically only 15 to 20%, it is likely that, the major portion of the applied magnesium fertilizer is adsorbed (fixed) to soils at their adsorption sites. Hence, application of magnesium fertilizer based on only agronomic soil test without the due consideration of magnesium adsorption capacity of each soil will end up being a flaw. To this end, it became necessary to study the adsorption of magnesium in soils in order to determine the maximum adsorption and buffering capacity of each soil for magnesium cation.

Adsorption equations

Several physicochemical equations were used, based on experimental foundations and concepts, to describe the adsorption of magnesium in different soil systems. The constants of these equations were used to predict the availability of magnesium and the supply capacity of the soil, as well as its need by plants [18, 19, 20 and 21]. These equations are:

Langmuir equation

This equation is distinguished from other equations in that it expresses the maximum limit of adsorption with complete saturation of the monolayer of the element under study on all sites of the adsorbed surface, and adsorption is at a constant energy for the exchange sites on the adsorbent surface (surfaces of chemically active colloids). It also describes adsorption with high efficiency at concentrations. Low levels of cadmium, lead, and zinc [22].

This equation was used by a number of researchers to describe the adsorption of potassium, iron, copper and boron [23, 24, 25, 26, 27, 28 and 29].

This equation has been used by a number of researchers to describe the adsorption of magnesium, and [16] stated that the Langmuir equation is the most appropriate in describing the adsorption of magnesium. [18] also found that the Langmuir equation was the best in describing the adsorption of magnesium in three soils planted with rice in Malaysia, compared to the Freundlich and Temkin equations, which were not suitable in describing the adsorption of magnesium.

Ferundlich equation

The Freundlich equation is one of the physicochemical equations used to describe the adsorption of nutrients such as phosphorus, zinc, copper, manganese, iron, manganese and boron [30, 31, 32, 33, 34 and 35]. It is one of the empirical equations, as it is mainly based on the adsorption model, which indicates that the binding strength decreases as the element increases or the coverage of the effective adsorption sites increases [36]. Studies have indicated the suitability of this equation in describing magnesium adsorption in soils [18, 19, 20 and 21].

Temkin equation

This equation was used in a limited degree in the description of analogy with some elements such as zinc, boron, iron and phosphorus [37 and 33], and was not used in the description of magnesium gaskets in the unveiled leaks systems due to its incompetence compared to the equations of [21]. This equation assumes that the binding energy decreases linearly with increasing adsorption of the element.

Due to the few studies related to the adsorption of magnesium in Iraqi soils, the study aimed to use these equations to describe the course of the physicochemical reactions of magnesium and the relationship of adsorption standards to some soil characteristics.

Soil samples

Five soils were selected and are agriculturally exploited for several agricultural seasons from the sites of Al-Jadriya, Al-Youssoufia, Wasit, Baqubah, and Karma. Twenty soil samples were taken from each site from a depth of 0-15 cm, then mixed to obtain a composite sample. They were air dried, ground, and sieved using a sieve with holes diameter of 2 mm. The soil of the above sites was analyzed physically and chemically, and the results are shown in Table 1 according to the methods adopted by [38], while active carbons were estimated according to the [39].

Magnesium adsorption

In order to evaluate the adsorption of magnesium ions in the study soil, a weight of 10.2696 grams of hydrated magnesium sulphate ($MgSO_4.7H_2O$) was used and dissolved in a liter of 0.01 M calcium chloride $CaCl_2.2H_2O$ to obtain a standard solution with a concentration of 1000 mg Mg L^{-1}, then a series of standard solutions were prepared from it. It has eight concentrations: 0, 100, 120, 140, 160, 200, 180, and 220 mg Mg

Table 1. Some chemical and physical properties of soils.

Property		Al-Jadriya	Baqubah	Al-Youssoufia	Al-Karma	Wasit	Unit
$EC_{1:1}$		3.21	4.30	6.63	5.82	2.96	dS m^{-1}
$pH_{1:1}$		7.46	7.60	7.36	8.31	7.64	
O.M		11.2	12.0	3.28	4.6	6.8	g kg^{-1} soil
Carbonate minerals		220.0	345.0	318.0	328.0	238.0	
Active carbonate M.		88.3	126.2	107.9	114.7	93.8	
CEC		11.2	26.4	17.3	23.8	14.2	C $mol_{+}kg^{-1}$ soil
Soluble ions	Ca^{2+}	9.12	10.50	16.45	8.70	7.25	m mole L^{-1}
	Mg^{2+}	4.71	7.50	7.13	3.60	4.42	
	Na^{+}	3.73	5.70	39.65	21.40	5.85	
	K^{+}	1.03	0.80	5.08	1.30	0.94	
	CO_3^{2-}	-	-	-	-	-	
	HCO_3^{-}	2.14	2.80	6.20	3.10	1.90	
	SO_4^{2-}	4.65	12.90	18.15	7.40	9.20	
	Cl^{-}	20.11	14.40	36.64	7.40	9.10	
Available nutrients	N	26.31	16.23	9.00	7.40	31.60	mg kg^{-1} soil
	P	6.30	7.34	3.25	6.30	14.80	
	K	175.0	187.0	215.0	176.0	181.0	
	Mg	81.4	292.3	270.0	140.0	39.9	
Particle size analysis							
Clay		124.0	187.5	335.0	300.0	76.0	g kg^{-1} soil
Silt		116.0	762.5	533.8	438.0	365.0	
Sand		760.0	250.0	131.2	262.0	559.0	
Texture		Sandy loam	Silt loam	Silty Clay Loam	Clay loam	Sandy loam	

L-1. The resulting concentrations were 0, 1000, 1200, 1400, 1600, 1800, and 2000 And 2200 mg Mg kg-1 of soil for eight samples from each soil separately, and 0.5 ml of toluene was added to it in order to inhibit the activities of soil organisms. The soil suspensions were shaken at a constant temperature of 298±2 K in 250 ml centrifuge bottles. in a shaker with a speed of 175 (opm) for 16 h [20]. A weight of 2 grams of dry soil (from each of the five sites separately)

Physicochemical adsorption equations

The mathematical formulas for the equations used are described in [40] and are as follows:

* Langmuir equation $C/X = 1/Klb + C/b$
* Freundlich equation $\ln X = \ln Kf + 1/n \ln C$
* Temkin equation enables $X = Kt + B \ln C$

Since:

C: Iron concentration at equilibrium

X: amount of iron adsorbed

ln: natural logarithm

n :and Kf: constants of the Freundlich equation

B and Kt: Temkin equation constants

Kl: bond strength according to the Langmuir equation

b: Maximum adsorption according to the Langmuir equation

To determine the efficient equation, several statistical indicators were adopted: the simple correlation coefficient r, the determination r2, the value of t, and the standard error of estimate (SE.e.), and simple regression and nonlinear regression equations were used according to [41].

Results and Discussion

Magnesium adsorption

The results shown in Table 2 showed that the Freundlich equation was the most efficient equation used in this study to evaluate the adsorption of magnesium and its content in the soil solution at dynamic equilibrium in the five soils under study because it had the highest value of the correlation coefficient r and the coefficient of determination, the highest value of t, and the lowest value of the estimated standard error of 0.982, 0.964, 23.115, and 0.080, respectively, while the order of efficiency of the Langmuir equation was after the Freundlich equation in describing magnesium adsorption. This is because it has a correlation coefficient of 0.980, a coefficient of determination of 0.957, t value of 12.921, and an estimated standard error of 0.179, while the enabling equation was less efficient with a correlation coefficient of 0.883, a coefficient of determination of 0.781, t value of 4.480, and the highest estimated standard error of 3.908. The relationship between magnesium adsorption and its content in the soil solution was significant at the level p ≤0.01)) for all equations used. Although the Freundlich equation was superior in describing the adsorption of magnesium, the Langmuir equation was also good, and it is followed by an equation that enables both the Langmuir and Freundlich equations to have approximately equal constants through which the greatest adsorption and desorption strength can be described, so it can be adopted in this study. The efficiency of the physicochemical equations in describing the course of magnesium adsorption reactions can be arranged according to the following: Freundlich > Langmuir > Temkin, as these efficiency reached (R^2 x100) in the order of 96.4, 95.7, and 78.1% (Table 2).

The results of the study are consistent with a number of studies that found that the Freundlich equation was the most

and the highest estimated standard error of 3.908. The relationship between magnesium adsorption and its content in the soil solution was significant at the level

efficient in describing magnesium adsorption to five soil samples in Nigeria [19 and 20].

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The results of the study are consistent with a number of studies that found that the Freundlich equation was the most efficient in describing magnesium adsorption to five soil samples in Nigeria [19 and 20].

Table 2. Statistical indicators of magnesium adsorption in soil according to physicochemical equations (n =8).

location	Freundlich equation				Langmuir equation				Temkin equation			
	r	*R²*	t value	*Std. Error of Estimate* (SE.e)	*r*	*R²*	t value	*Std. Error of Estimate* (SE.e)	*r*	*R²*	t value	*Std. Error of Estimate* (SE.e)
Al-Jadriya	0.969	0.940	8.833	0.087	0.983	0.967	12.032	0.038	0.934	0.873	5.863	3.816
Baqubah	0.999	0.998	57.978	0.004	0.976	0.953	10.097	0.194	0.858	0.736	3.738	4.685
Al-Youssoufia	0.975	0.951	9.891	0.165	0.995	0.990	22.118	0.217	0.927	0.859	5.525	2.170
Al-Karma	0.969	0.938	8.713	0.113	0.984	0.968	12.254	0.284	0.816	0.666	3.154	4.080
Wasit	0.997	0.995	30.161	0.029	0.964	0.929	8.105	0.164	0.879	0.772	4.119	4.799
Mean (X)	0.982	0.964	23.115	0.080	0.980	0.957	12.921	0.179	0.883	0.781	4.480	3.908

*The values of r, r2 and t significant at 0.01 level.

Table 3. Constants of the Freundlich equation and values of maximum adsorption b and binding strength K for Mg ion according to the Langmuir equation of study soils.

Location	Freundlich equation		Langmuir equation	
	Ln K_f	1/n	B	K

			mg Mg kg^{-1} soil	ml Mg mg^{-1}
Al-Jadriya	0.058	0.987	350.00	0.047
Baqubah	3.783	0.007	950.00	0.005
Al-Youssoufia	10.026	3.010	620.50	0.003
Al-Karma	4.435	1.817	880.50	0.003
Wasit	0.986	1.213	450.00	0.084
Mean (X)	3.858	1.425	710.20	0.042
Correlation coefficient (r)	0.780*		0.961**	

*and ** significant at the 0.05 and 0.01 levels.

Table 4. Correlation coefficient(r) between the constants of the Freundlich and Langmuir equations of study soils. Binding strength

Freundlich equation	Langmuir equation	
	Maximum adsorption (b)	Binding strength (K)
Ln K_f	-0.908*	0.684 –ns
1/n	-0.883*	-0.668 ns

[21] also found that the Langmuir and Freundlich equations were appropriate in describing the adsorption of magnesium in soil. While [18] found that the Langmuir equation was superior in describing the adsorption of magnesium in soil from Malaysia.

The results shown in Table 4 indicated the effect of the five soils used in the study on their adsorption of magnesium from magnesium added at concentrations within the range (2200 - 1000 mg Mg kg-1 soil). It was noted from these results that the constants of the Langmuir equation calculated according to the linear regression technique, were linked together and showed results of regression analysis: There is a negative linear relationship at the level ($p \leq 0.01$) between the adsorption coefficient lnKf with the constant 1/n for the soil under study, the correlation coefficient for that relationship reached (0.780*), and the constant of the Langmuir maximum adsorption equation, b, was significantly correlated with the binding strength K (r = 0.961**) (Table 3).

The results in Table 3 showed that the average constants of the Freundlich equation: the adsorption factor lnKf and the constant 1/n for the soils used in the study reached 3.858 and 1.425, respectively. As for the constants of the Langmuir equation, the average maximum adsorption b and the binding strength K reached 710.20 mg Mg kg-1 and 0.042 L mg-1 sequentially. Which indicates that the amount of magnesium adsorbed from the five soils amounted to 32.3% of the magnesium added in the form of $MgSO_4.7H_2O$, and that 67.7% remained free in the soil solution.

Figure 1. An example of graphs that should be inserted below the results and discussion section.

The results in Table 3 also indicated that the highest value of the adsorption coefficient according to the Freundlich equation lnKf was in the Al-Youssoufia soil and reached 10.026, while its lowest value was 0.058 in the Jadriya soil. In contrast, the second constant of the Freundlich equation is 1/n, which represents the linear regression coefficient for this equation, as its values reached 3.010 and 0.987 for the soils of Al-Youssoufia and Jadriya, respectively. The results in Table 3 showed adsorption coefficient lnKf according to the Freundlich equation with constant of the maximum adsorption Langmuir equation b (r = 0.908*) but not significant with binding that the highest value of the maximum adsorption b (Langmuir equation constant) was in the Baqubah soil, reaching 950.0, while it was the lowest in the Jadriya soil, reaching 350.0. The maximum adsorption in the Baqubah soil increased by 171.4 compared to the Jadriya soil.

Baqubah soil showed a higher capacity in the maximum adsorbed amount of magnesium compared to Al-Jadiriya soil, which is attributed to its higher content of total carbonate minerals, active carbons, cation exchange capacity (CEC), organic matter, and available magnesium (Table (2). [19 and 20] found the adsorption of magnesium according to the constants of the Freundlich equation was positively linearly correlated with the exchange capacity of positive ions and the organic matter content. [18] found that the adsorption of magnesium according to the Freundlich and Langmuir equations was positively linearly correlated with pH (r = 0.948).

The results of the simple linear regression analysis also showed that there is a positive significant relationship at the level of (0.05 and $p \leq 0.01$) between the strength K. Also a correlation relationship was also found between the second constant of the Freundlich equation 1/n with the maximum adsorption Langmuir equation b (r = 0.883*) Table 4, It appears from the results that the constants of the Freundlich equation can be used Also, as in the Langmuir equation.

The results of the regression analysis also showed in Table 5 the presence of a significant linear relationship at the level of (0.05 and $p \leq 0.01$) between the maximum adsorption b according to the Langmuir equation and some of properties study soil. It was positive with both the organic matter content and cation exchange capacity CEC, total and active carbonate content and content of available magnesium. The correlation coefficient values reached 0.969**, 0.974**, 0.884*, 0.976**, and 0.931*, respectively. This has been confirmed by several studies indicating the retention of magnesium in limestone soils due to chemically active carbonate minerals and a decrease in its availability for plants [18, 19 and 20]. [34] also found a linear relationship between the maximum iron adsorption according to the Langmuir equation with the electrical conductivity and the content of total and active carbons and available iron in the six soils of his study. Several studies have confirmed with

Table 5. Linear relationship between maximum magnesium adsorption b according to theLangmuir equation (Y) and soil properties (X).

Soil properties	Regression equation	Correlation coefficient (r)
EC	Y = 178.630 – 18.893 X	-0.851
pH	Y= 293.742 – 26.286 X	-0.275
Organic matter (O.M)	Y = 24.808 + 8.872 X	0.969**
CEC	Y = -31.379 + 5.522 X	0.974**
Total carbonate	Y = -92.704 + 0.566 X	0.884*
Active total carbonate	Y= -172.757 + 2.298 X	0.976**
Silt	Y = 101.453 – 0.021X	-0.141
Clay	Y = 145.203 – 0.260 X	-0.811
Available Mg	Y = 21.692 + 0.301 X	0.931*

*and ** significant at the 0.05 and 0.01 levels.

regard to the adsorption of iron, zinc, and boron [23, 33, 42 and 43]. As for the other soil properties, their effect on the adsorption of magnesium was not significant (Table 5). The maximum adsorption of magnesium, which indicates the maximum amount of magnesium adsorbed in the soil, is not sufficient evidence of the availability of magnesium. Rather, the binding strength is what determines this. The soil of Baqubah, although it has the maximum adsorption of magnesium compared to other soils, its binding strength is low, which means that most Adsorbed magnesium is available in it.Conclusion It is concluded from this study that the Freundlich equation was the most efficient and that both the Freundlich and Langmuir equations gave a good description in describing the adsorption of magnesium in all soils of the study and that the susceptibility of the soils to the adsorption of magnesium was as follows: Baqubah > Al Karma > Al-Youssoufia > Wasit > Al-Jadriyah and that the adsorption of magnesium is affected Some soil characteristics (CEC, organic matter content, total and active carbonate, and available magnesium.

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