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PJBS

ISSN 1028-8880

Pakistan Journal of Biological Sciences

ANSInet
Asian Network for Scientific Information
308 Lasani Town, Sargodha Road, Faisalabad - Pakistan

Pakistan Journal of Biological Sciences 6 (15): 1376-1379, 2003
ISSN 1028-8880

Magnesium Adsorption Behaviour of Three Malaysian Rice Soils

[1]A.T.M.A. Choudhury and Y.M. Khanif
Department of Land Management, Faculty of Agriculture,
Universiti Putra Malaysia, 43400 UPM, Serdang, Selangor, Malaysia,
[1]SUNFix Centre for Nitrogen Fixation, School of Land, Water and Crop Sciences,
Ross Street Building A03, The University of Sydney, NSW 2006, Australia

Abstract: A study on magnesium (Mg) adsorption was carried out in three Malaysian rice soils (Guar, Hutan and Kangar series) using six levels of Mg (0, 46.3, 54.0, 61.7, 69.4 and 77.2 mmol kg^{-1}). The Langmuir, Freundlich and Temkin adsorption equations were fitted to the Mg adsorption data. Magnesium adsorption by the Guar and Kangar soils but not the Hutan soil was described well by the Langmuir equation. Magnesium adsorption by the Kangar soil was well described also by the Freundlich and Temkin equations whereas the adsorption data in other two soils did not fit these equations. A significant correlation was found between Mg adsorption and soil pH, while there was no correlation between Mg adsorption and either organic matter content or cation exchange capacity. These results indicated that Mg adsorption is mainly dependent on soil pH. In soils with a higher adsorption capacity, more Mg fertilizer may be needed to get an immediate crop response.

Key words: Adsorption, magnesium, rice soils

Introduction

Magnesium (Mg) is an essential element for all crops including rice. Magnesium requirement for a rice crop is about 4 kg for the production of one tonne of rough grain including straw (De Datta, 1981; Sahrawat, 2000). A low supply of Mg depresses rice yield and causes iron toxicity syndrome on strongly acid soils (Ponnamperuma and Deturck, 1993). Investigations showed that rice yields increase significantly due to Mg application (Vijayalakshmi and Mathan, 1994; Choudhury and Khanif, 2001, 2002a). The largest rice growing area of Malaysia is located in the Muda Irrigation Scheme, Kedah. A recent investigation showed that Mg deficiency exists in many sites of this irrigation scheme (Choudhury and Khanif, 2000a). Therefore, Mg fertilization is important to meet the Mg requirement of rice crops grown in this area.

When fertilizer Mg is applied to the soil, much of it is adsorbed by the soil colloids. Sorption phenomena involved may include electrostatic attraction, covalent bonding or isomorphous replacement in the crystal lattice (Ponnamperuma, 1978). These sorption phenomena depend on soil characteristics (Choudhury and Khanif, 2000b). The variation in Mg adsorption among soils (Phillips *et al.*, 1986) suggests that knowledge of Mg adsorption behaviour will be a valuable guide to the application of Mg fertilizer. This study was undertaken to determine the Mg adsorption behaviour of three rice soils, varying in pH, organic matter content and cation exchange capacity.

Materials and Methods

Three soils (Guar, Hutan and Kangar series) were used in the study. A description of the soils is presented in Table 1. The mineralogical class of the Hutan series is kaolinitic, whereas it is mixed for the other two soils (Paramananthan, 1998). The clay fraction of the Hutan series is mainly composed of kaolinite with low amount of smectite. Kaolinite, smectite, micas and traces of quartz are present in the clay fraction of both the Guar and Kangar series (Azmi, 1982).

Soil samples (0-15 cm depth) were collected from rice growing areas under the Muda Irrigation Scheme, Kedah, Malaysia. The samples consisted of two marine alluvial and one riverine alluvial soils. The soils were air dried, ground and sieved through a 2 mm sieve. Soils were analysed for organic matter, pH, cation exchange capacity (CEC), total N, available P, exchangeable K, Mg and Ca and available Zn and Cu. Properties of the soils are given in Table 2. Organic matter was determined by the potassium dichromate and H_2SO_4 digestion method (Walkley and Black, 1934). Soil pH was measured in water by the glass electrode (Peech, 1965). Total N was determined by the sulphuric-salicylic acid digestion method (Bremner and Mulvaney, 1982). Available P was determined by the NH_4F-HCl extraction method (Bray and Kurtz, 1945). Cation exchange capacity, exchangeable K, Mg and Ca were determined by the ammonium acetate extraction method (Schollenberger and Simon, 1945). Available Zn and Cu were determined by atomic

Table 1: Description of the soils used for the study

Soil series	Location	Taxonomy (Source: Paramananthan, 1998)	Parent material
Guar	Teluk Cempedak	Typic Sulfaquept, very fine clayey, mixed, isohyperthermic, brown.	Marine alluvium
Hutan	Gajah Mati	Aeric Plinthic Kanahaplaqualt,fine clayey, kaolinitic, isohyperthermic, pallid.	Riverine alluvium
Kangar	Batu Pahat	Typic Endoaquert, very fine clayey, mixed, isohyperthermic, pallid.	Marine alluvium

Table 2: Selected properties of the soils used for the study

Properties	Guar	Hutan	Kangar
Organic matter (%)	5.61	1.82	1.99
pH	3.2	3.6	7.5
Cation exchange capacity (cmol kg^{-1})	13.48	7.15	9.13
Total N (%)	0.16	0.07	0.06
Available P (mg kg^{-1})	6.8	31.1	3.6
Exchangeable K (cmol kg^{-1})	0.32	0.13	0.08
Exchangeable Mg (cmol kg^{-1})	0.29	0.09	0.34
Exchangeable Ca (cmol kg^{-1})	2.09	1.93	8.11
Available Zn (mg kg^{-1})	1.58	2.99	0.08
Available Cu (mg kg^{-1})	0.15	3.10	0.04

absorption spectrophotometry following extraction with 0.05 *N* HCl (Ponnamperuma *et al.*, 1981).

Four g of each soil were weighed into different centrifuge tubes. Different concentrations of Mg solutions (0, 150, 175, 200, 225 and 250 mg Mg $liter^{-1}$) were prepared by dissolving magnesium chloride ($MgCl_2.6H_2O$) in distilled water. Thirty milliliters of Mg solution with different concentrations were added to 4 g soil in centrifuge tubes to obtain 0, 46.3, 54.0, 61.7, 69.4 and 77.2 mmol kg^{-1} of added Mg. Each treatment was replicated three times. The experiment was conducted using a completely randomized design. The tubes were covered tightly and incubated at room temperature (25-30°C) for 15 days, which has been shown in preliminary studies to be sufficient for an equilibrium condition for Mg adsorption to be attained in these soils.

After 15 days, the tubes were centrifuged and the supernatant solutions were filtered and analysed for Mg by atomic absorption spectrophotometry. Solution Mg concentrations were calculated as milli mole per liter (mmol $liter^{-1}$). The amount of Mg adsorbed per gram of soil (x/m) was calculated from the difference in Mg concentration in the initial added Mg solution and the supernatant equilibrium solution © taking into account the amount of Mg present in solution in the control (no Mg) treatment. The adsorbed Mg was calculated as milli mole per kg (mmol kg^{-1}). Adsorption data were correlated with pH, cation exchange capacity and organic matter content of the soils. The Mg adsorption data in the soils were fitted into following adsorption equations:

Langmuir adsorption equation: $c/(x/m) = 1/kb + c/b$ [1]

where: c is the equilibrium solution Mg concentration (mmol $liter^{-1}$), x/m is the mass of Mg adsorbed per unit mass of soil (mmol kg^{-1}), k is a constant related to bonding energy of Mg to the soil, b is the maximum Mg adsorption capacity (mmol kg^{-1}) of the soil. A plot of c/(x/m) versus c gives a straight line. The values of b and k are obtained from the slope (1/b) and the intercept (1/kb), respectively.

Freundlich adsorption equation: $x/m = ac^b$ [2]

By rearranging: $\text{Log } (x/m) = \log a + b \log c$ [3]

where: x/m is the mass of Mg adsorbed per unit mass of soil (mmol kg^{-1}), c is the equilibrium solution Mg concentration (mmol $liter^{-1}$), a and b are constants. A plot of log (x/m) versus log c gives a straight line. The values of a and b are obtained from the intercept (log a) and slope (b), respectively.

Temkin adsorption equation: $x/m = a + b \ln C$ [4]

where: x/m is the mass of Mg adsorbed per unit mass of soil (mmol kg^{-1}), c is equilibrium solution Mg concentration (mmol $liter^{-1}$), a and b are constants. A plot of x/m against ln c gives a straight line. The values of a and b are obtained from the intercept (a) and the slope (b), respectively. The b value of Temkin equation is considered as the Mg buffering capacity (retention capacity of adsorbed Mg) of soil (mmol kg^{-1}).

The necessary statistical analysis of the data were done using the Statistical Analysis System (SAS., 1987).

Results

The equilibrium solution Mg concentration increased linearly with increasing level of added Mg in all the three soils (Fig. 1). However the rate of increase was the highest in the Guar soil, intermediate in the Hutan and the least in the Kangar soil. Correlation analysis indicated that the relationship between Mg adsorption and soil pH was positive and significant (r = 0.948), while there was no significant relationship between Mg adsorption and either organic matter content (r = - 0.255) or cation exchange capacity (r = 0.012). The Mg adsorption data from the Kangar soil fitted the Langmuir, Freundlich and Temkin adsorption equations well (Table 3) while adsorption data in the Hutan soil fitted none of the adsorption equations. Magnesium adsorption by the Guar soil was described by

Table 3: Regression equations and R^2 values for the Langmuir, Freundlich and Temkin adsorption isotherms for Mg adsorption in the soils under study

Soil	Adsorption isotherm	Regression equation	R^2 value
Guar	Langmuir	y = - 0.0226 + 0.0445x	0.9354ns
	Freundlich	y = 1.5276 – 0.1761x	0.3232ns
	Temkin	y = 33.235 – 4.7694x	0.3381ns
Hutan	Langmuir	y = 0.1228 + 0.021x	0.5611ns
	Freundlich	y = 0.9961 + 0.4911x	0.6158ns
	Temkin	y = 4.2625 + 11.11x	0.6343ns
Kangar	Langmuir	y = 0.0276 + 0.0175x	0.9555**
	Freundlich	y = 1.4068 + 0.3403x	0.8488*
	Temkin	y = 23.438 + 12.632x	0.8509*

**= Significant at 1% level, *= significant at 5 % level, ns = non-significant

Table 4: Buffering capacity, maximum adsorption capacity and constant of energy of adsorption for Mg adsorption in the soils under study

Soil	Buffering capacity[a] (mmol kg^{-1})	Maximum adsorption capacity[b] (mmol kg^{-1})	Constant of energy of adsorption[c] (k value)
Guar	-	22.5	- 1.97
Kangar	12.6	57.1	0.63
Hutan	-	-	-

[a]Calculated b value from the Temkin equation, [b]calculated b value from the Langmuir equation, [c]calculated k value from the Langmuir equation
In the Guar series, adsorption data did not fit the Temkin equation
In the Hutan series, adsorption data did not fit either the Langmuir or Temkin equations

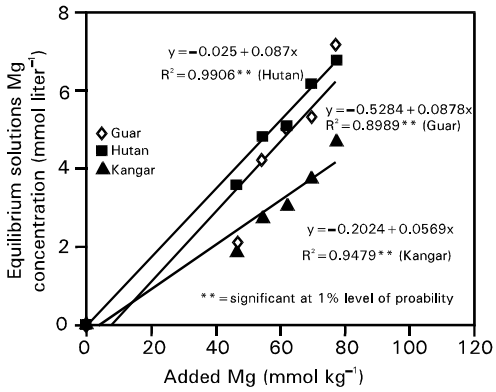

Fig. 1: Effect of Mg addition on equilibrium solution Mg concentration of the soils

the Langmuir equation only (Table 3). The Maximum Mg adsorption capacity calculated from the Langmuir equation, was 22.5 mmol kg^{-1} in the Guar soil while it was 57.1 mmol kg^{-1} in the Kangar soil (Table 4). The constant K, which was derived from the Langmuir equation and is a measure of energy of adsorption, was – 1.97 in the Guar soil while it was 0.63 in the Kangar soil (Table 4). The b, value which was derived from the Temkin equation and provides a measure of Mg buffering capacity (retention capacity of adsorbed Mg), was 12.6 mmol kg^{-1} in the Kangar soil.

Discussion

Variations in equilibrium solution Mg concentration among soils were attributed to the differences in Mg adsorption. Differences in equilibrium solution Mg concentration among soils were found in a previous investigation (Ashraf and Biddappa, 1994). In a previous investigation, Nakahara and Wada (1994) reported that Mg adsorption increases with increasing pH. At higher pH, negative charge of the soil increases providing an increased number of exchangeable sites with a higher affinity for divalent cations (Chan *et al.*, 1979). This may explain the significant correlation between Mg adsorption and pH. As adsorption data in the Hutan soil did not fit Langmuir equation, maximum adsorption capacity and K value were not obtained for this soil. As maximum Mg adsorption capacity is higher in the Kangar soil over the Guar soil, diffusion of Mg would be slower in the Kangar soil compared to the Guar soil. The lack of fit of the adsorption with the Temkin equation meant that an estimate of Mg buffering capacity was not possible for either the Guar or the Hutan soil. The Langmuir equation is derived based on the assumption that there is a constant energy of adsorption, which is independent of surface coverage. This situation does not occur always in nature (Bohn *et al.*, 1979). This may explain the failure of the Mg adsorption data for the Hutan soil to conform the Langmuir equation. The inability of the Langmuir equation to describe the Mg adsorption data in the Hutan soil, may indicate that there are several discrete types of Mg sorption sites each with a different selectivity for Mg. Similar results have been reported for many soils regarding K adsorption (Dufey and Delvaux, 1989; Pal *et al.*, 1999).

Farmers are not practicing Mg fertilization in the Muda Irrigation Scheme. Investigations have shown that rice crops grown in this irrigation scheme suffer from Mg deficiency in many locations (Samy *et al.*, 1992; Choudhury and Khanif, 2001, 2002b; Choudhury *et al.*, 2002). Magnesium fertilization should be done based on soil Mg status and adsorption characteristics to overcome this problem. All the three soils used in this study are deficient in Mg (Table 2). Magnesium contents in the soils are below the critical deficiency level of 0.40 cmol kg^{-1} (Choudhury and Khanif, 2000a). Magnesium fertilizer application is necessary in these soils to meet the crop demand. As maximum Mg adsorption capacity is higher in the Kangar soil compared to the Guar soil, more Mg fertilizer may be needed in the Kangar soil compared to the Guar soil to get an immediate crop response.

The findings of this study indicate that Mg adsorption varies amongst the three soils studied. Maximum adsorption capacity is higher in soil with higher pH. In soils with higher adsorption capacity, more magnesium fertilizer may be needed to get an immediate crop response.

Acknowledgments

The authors are grateful to the National Council for Scientific Research and Development of Malaysia for financial support under the project on Intensification of Research in Priority Areas (IRPA).

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