Effect of pH and Organic Matter on Monovalent-Divalent Cation Exchange Equilibria in Medium Textured Soils

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ABSTRACT

A study was accomplished to investigate the effect of organic matter and pH on cation exchange equilibria in soils. The physical and chemical properties like pH_s, EC_e, soluble ions, exchangeable cation, SAR, ESP, BCSP and CEC of two medium textured soils were determined. In homovalent exchange the K_k values increased with an increase in organic matter and pH in both the soils. Kerr, Vanselow and Gapson's coefficients were calculated. In heterovalent exchange Ca^{2+} over Na^+ replacement decreased and hence the values of all the coefficients also decreased with an increase in organic matter and pH in both the soils.

Key Words: Cation exchange; Adsorption; pH; Organic matter; Medium textured soil

INTRODUCTION

The cation exchange process in soils is of great importance to the nutrition of plants. This phenomenon is better understood with the growth of soil chemistry and genetic aspects of soils.

Cation exchange is important in sustaining soil fertility, in causing and correcting soil acidity and basicity, in changes altering soil's physical properties and as a mechanism in purifying or altering percolating waters.

Several cation exchange equations are used to evaluate the contribution of exchangeable cations for nutrient supply. The primary difference between various cation exchange equations is their different assumptions about the activities of exchangeable cations. Kerr (1928) used concentration of cations in place of their activities for homovalent cation exchange. Vanselow (1932) assumed that activities of adsorbed cations were proportional to their mole fractions, which hold good for both homovalent as well as heterovalent cation exchange. Whereas, Gapon (1933) used concentration for adsorbed cations and activities for soluble cations. However various factors could alter the exchange coefficients of these equations like pH, organic matter, concentration, soil CEC and temperature.

Keeping this in view, present study was planned with the objective, to study the effect of organic matter and pH on Kerr Vanselow and Gapon coefficients in medium textured soils.

MATERIALS AND METHODS

Two soil samples one sandy loam (soil A, Pendorian soil series) and other loamy clay (soil B, Hafizabad soil series) both having medium texture were collected. Both the soil samples were processed and analyzed by the methods of U.S. Salinity Laboratory Staff (USSLS, 1954) and Moddie *et al.* (1954) (Table I). Particle size analysis was made by Bouyoucos hydrometer method (Bouyoucos, 1962) and for textural class International Textural Triangle was followed.

Table I. Physico-Chemical characteristics of soils

Soil characteristics	Pendorian Soil series	Hafizabad soil series
Clay %	17	25
Textural class	Sandy loam	Loamy clay
pH_s	7.07	7.50
EC_e (dS m^{-1})	0.95	4.47
TSS (mmol$_c$ L^{-1})	9.5	44.7
SAR (mmol L^{-1})$^{1/2}$	3.11	12.94
Exchangeable Cations		
Na$^+$ (Cmol$_c$ kg^{-1})	2.11	2.95
K$^+$ (Cmolc kg^{-1})	0.14	0.41
(Ca^{2+}+ Mg^{2+}) (Cmol$_c$ kg^{-1})	3.77	9.33
CEC (Cmol$_c$ kg^{-1})	6.02	12.69
ESP %	35.04	23.25
BCSP %	100	100
Organic carbon %	0.30	0.90
Organic matter %	0.52	1.55

Both the soil samples were treated with NH_4Cl solution to remove all the cations present in the soils. After three washings with ethanol, soil samples were made homoionic with $CaCl_2$ solution. For homovalent exchange, adsorbed, Ca was replaced with $CaCl_2$: $MgCl_2$ (1:1) solution while for heterovalent exchange the Ca-saturated samples treated with $CaCl_2$:NaCl (1:1) solution. The pH levels for soil A were 7.07 control 8.0 ±1.0 and 9.0 ±1.0 while these were 7.5 (control), 8.0 ±1.0 and 9.0±1.0 for soil B. Organic matter was 0.52% (control) in soil A and 1.55% (control) in soil B. To get organic matter (2 & 4%) over and above the control value, well rotten farmyard manure was added in both

the soils. NaOH and HCl were used to maintain the pH. Desorbed cations were determined in the filtrates. Following equations were tested by calculating the exchange coefficient.

1. Kerr equation

a. For divalent-monovalent exchange

$$K_k = \frac{[NaX]^2 [Ca^{2+}]}{[CaX][Na^+]^2} = \frac{(NaX)^2 (Ca^{2+})}{(CaX)(Na^+)^2}$$

b. For divalent-divalent exchange

$$K_k = \frac{[MgX]^2 [Ca^{2+}]}{[CaX][Mg^{2+}]} = \frac{(MgX)(Ca^{2+})}{(CaX)(Mg^{2+})}$$

2. Vanselow equation

a. For divalent-monovalent exchange

$$K_V = \frac{[NaX]^2 (Ca^{2+})}{[CaX][NaX+CaX](Na^+)^2}$$

b. For divalent-divalent exchange

$$K_V = \frac{[MgX][Ca^{2+}]}{[CaX](Mg^{2+})}$$

3. Gapon Equation

a. For divalent-monovalent exchange

$$K_G = \frac{[NaX](Ca^{2+})^{0.5}}{[CaX]^{0.5}(Na^+)}$$

[ ] = concentration of cations; ( ) = Activity

RESULTS AND DISCUSSION

Physico-chemical properties showed that CEC of soil B was greater than that of soil A (Table I), due to higher organic matter in the former soil. The high CEC and organic matter attracts strongly the polyvalent cations that reduces their exchange by low valent cation like Na$^+$ (Rengasamy & Olsson, 1991).

pH increase the CEC due to increase of charge density. As the pH increased the negative charge also increased which ultimately increased the adsorption of Ca^{2+}- Mg^{2+} (Murtaza, 1997).

It is apparent that Ca^{2+} preference increased as the pH increased from 7 to 8 in both the soils. The increase in value of selectivity coefficient of soil B is more than that of soil A because soil A has low CEC than soil B. Greater replacement of Ca^{2+} with Mg^{2+} is in accord with the concept that in homovalent system the preferentially adsorbed ion is usually the ion with smaller hydrated radius (Helfferich, 1962).

Both the soils showed different values of selectivity coefficient, due to low CEC of soil A compared to soil B. The low CEC soils are easily accessible to the cations with greater hydrated radii compared to high CEC soils to become neutral. Overall, it could be concluded that K$_k$ value for Ca^{2+} - Mg^{2+} exchange differed not only from treatment to treatment but also from soil to soil having different soil properties.

Ca^{2+} - Na$^+$ Exchange. In divalent-monovalent exchange the K$_v$ values ranges from 0.00043 to 0.00299 for soil A and from 0.000099 to 0.00398 for soil B (Table III). In Ca^{2+} - Na$^+$ exchange, as pH and organic matter increased, the values of selectivity coefficient K$_k$, K$_v$ and K$_G$ decreased because pH is considered to give additional negative charge resulting in higher CEC that favour preferential adsorption of Ca^{2+} over Na$^+$. Calcium preference over sodium increased with increase of pH. Specificity of adsorption of Ca^{2+} vs Na$^+$ might be related to the chemical nature of the negative charge on some of the exchangers in the soil as well as to the surface charge density. (Pratt *et al.*, 1962).

An increase in organic matter decreased the K$_k$, K$_v$ and K$_G$ values. CEC of both the soils increased with the increase of organic which ultimately increased the Ca^{2+}

Table II. Organic matter and pH effects on Ca^{2+} - Mg^{2+} exchange in soils

Trt.	Soils	Levels	Equilibrium solution		[Ca^{2+}] [Mg^{2+}]	Adsorbed bases		[MgX] [CaX]	Equilibrium constant
			Ca^{2+} (me L^{-1})	Mg^{2+} (me L^{-1})		CaX (me 100g^{-1})	MgX (me 100g^{-1})		Kerr
pH	A	7.07 (control)	1000	1200	0.833	1.94	1.76	0.9072	0.76
pH	A	8	1200	300	4.00	2.60	1.80	0.6923	2.77
pH	A	9	1400	350	4.00	1.56	1.64	1.0513	4.21
pH	B	7.50 (control)	1500	1500	1.000	3.0	2.0	0.660	0.66
pH	B	8	1450	650	2.231	2.1	1.2	0.571	1.27
pH	B	9	1500	700	2.140	3.0	3.5	1.169	2.49
OM	A	Control	1000	1200	0.83	1.94	1.76	0.9072	0.76
OM	A	2%	1100	245	4.50	8.10	1.66	0.2049	0.92
OM	A	4%	1550	250	6.20	2.10	1.10	0.5248	3.25
OM	B	Control	1500	1500	1.0	3.00	2.0	0.666	0.666
OM	B	2%	1400	450	3.1	1.96	3.4	1.730	5.36
OM	B	4%	1200	600	2.0	2.32	18	3.360	6.72

Trt = Treatment; OM= Organic matter

Ca^{2+} - Mg^{2+} Exchange. In Ca^{2+} - Mg^{2+} exchange under different soil conditions, the selectivity coefficient K$_K$ values ranged from 0.66 to 6.72 (Table II). An increase in pH and organic matter increased the K$_k$ of soil. The

preference. Increase in organic matter increased the surface charge density which attracted strongly the polyvalent cations and increased the preference of Ca^{2+} over Na$^+$.

Table III. Organic matter and pH effects on Ca^{2+} exchange in soils

Trt.	Soils	Levels	Equilibrium solution		Adsorbed		Equilibrium constants		
			Na$^+$ (me L^{-1})	Ca^{2+} (me L^{-1})	NaX me 100g^{-1}	CaX me 100g^{-1}	Kerr	Vanselow	Gapon
pH	A	7.07 (control)	851.32	650	4.348	1.30	0.0129	0.00228	0.10002
pH	A	8.00	932.61	800	4.000	2.20	0.0066	0.00106	0.0551
pH	A	9.00	884.78	650	2.5217	2.46	0.00215	0.00043	0.0295
pH	B	7.50 (control)	870.44	875	4.1131	3.00	0.00654	0.00092	0.046
pH	B	8.00	908.70	950	3.4435	3.10	0.0044	0.00067	0.037
pH	B	9.00	856.09	525	2.5348	5.70	0.00082	0.000099	0.012
OM	A	Control	666.52	675	5.4783	2.01	0.0224	0.00299	0.1061
OM	A	2%	620.87	600	5.9131	3.40	0.0165	0.00177	0.0686
OM	A	4%	932.61	800	4.000	2.20	0.00669	0.00107	0.0551
OM	B	Control	648.26	737.5	5.4783	1.85	0.0292	0.00398	0.1240
OM	B	2%	671.09	912.5	4.6087	2.60	0.0163	0.00226	0.0797
OM	B	4%	870.44	875.0	4.1131	3.00	0.0067	0.00094	0.0465

Trt = Treatment; OM= Organic matter

Organic matter in soils has been known to result in greater preference for Ca^{2+} than do clay minerals (Black, 1968). Overall, as organic matter increased the preference of exchange complex for Ca^{2+} also increased with the decrease of K_k, K_v and K_G values and showed preference of Ca^{2+} over Na$^+$.

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