Cation exchange capacity determination of soils with methylene blue exchange

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Abstract : Cation exchange capacity (CEC) determination of soils based on Methylene Blue (MB) sorption behaviour was investigated under appropriate conditions of concentration and equilibration for some selected classified soils collected from Purulia district of West Bengal and Cuttack district of Orissa. The CEC values measured by Methylene Blue – Tetrasodium Pyrophosphate (MB-TSPP) filter paper spot test titration method were found to be close to the values measured by conventional NH_4OAc method. The MB-TSPP filter paper spot test titration method was found to be highly suitable for rapid CEC determination of soils in field. A regression equation is also proposed for routine conversion of clay organic matter data into CEC for agricultural soils under Indian conditions.

Additional key words: *Cation exchange capacity, MB sorption, MB-TSPP spot test*

Introduction

The CEC of soils along with exchangeable bases provides a measure for soil fertility evaluation. The most reliable and widely used method of determination of CEC of acidic soils in laboratory is by saturation of the soil samples with neutral normal ammonium acetate (Schollenberger and Simon 1945).

A dye is a chemically stable coloured compound, the colour of which is due to chromophore and acidic or basic polar auxochromic groups (SO_3H, OH, NR_2, etc.) which essentially intensify the colour by virtue of Bathochromic shift (i.e. shifting of absorption band to longer wavelength in the visible range of the electromagnetic spectrum) and also make the dye water soluble. Methylene blue ($C_{16} H_{18}N_3SCl$) is a cationic dye, soluble in water and used for determination of cation exchange capacity and surface areas of clays (Bujdak *et al.* 1998).

Many research workers (Plesch and Robertson 1948; Bascomb 1964; Das and De 1982; Wang *et al.* 1996; Ana *et al.* 2000; Maged and Ulrich 2000) have worked with Methylene Blue in presence of different salts/chemicals related to chemistry of exchange/ adsorption of different cations leading to determination of cation exchange capacity.

However, such type of research has received very little attention in India. The rapidity and ease of the empirical method over the conventional, time consuming and tedious laboratory method certainly warrants critical evaluation of the former with respect to the latter. Moreover, one can also have some preliminary idea about CEC of the soils in field with very simple experimental exercise in the form of spot test. Therefore, the present investigation has been undertaken to evaluate and test the validity of MB – filter paper spot test titration method in some typical soils of West Bengal and Orissa.

Materials and Methods

Surface and sub-surface soil samples (Inceptisols, Alfisols and Entisols) were collected from Puruliya district of West Bengal and Cuttack district of Orissa. The soils were air dried, ground and passed through 2-mm sieve and analysed for some important physical and chemical properties (Table 1) following the procedure outlined in Jackson (1973). For neutral normal ammonium acetate CEC, 75 ml of $1(N)$ ammonium acetate was added to 10 g soil sample, stirred occasionally for one hour and kept overnight. The contents after filtration through Whatman No.1 filter paper were washed with 60 per cent ethyl alcohol to eliminate excess ammonium acetate. The soil mass was thereafter distilled with MgO for 40 minutes and the distillate was collected in 20 ml of 0.1 (N) H_2SO_4 with a few drops of methyl red indicator. The excess acid was back titrated with standard 0.1 (N) NaOH.

The rapid empirical MB-exchange capacities were determined following the procedure outlined by Wang et al. (1996). For the MB-acid filter paper spot titration test, 0.5 g soil sample was weighed into a 250 ml conical flask; 10 ml H_2O_2 (30 gL^{-1}) and 0.5 ml H_2SO_4 (2.5 M) were added and the mixture was gently boiled for 5 minutes and then diluted to 50 ml with distilled water. Methylene blue hydrochloride ($C_{16}H_{18}N_3SCl.3H_2O$) solution (0.01 M) was added with a micropipette to the flask. After each 0.5 ml addition, the contents of the flasks were swirled for about half a minute. A drop of liquid was taken from the flask and the suspension was placed on a filter paper. The end point of the titration was indicated by the appearance of the dye as a faint and distinct blue divergent halo surrounding the dyed solids. For the MB-TSPP titration, 0.5 g soil sample was transferred into a 250 ml conical flask containing 50 ml TSPP solution (20 gL^{-1}; pH $\approx$ 10). The mixture was boiled gently on a hot plate, then cooled to room temperature and then titrated with 0.01 (M) MB solution.

For the MB-H_2O titration method, 50 ml distilled water was added to get a sample suspension (without any soil pretreatment), followed by titration with MB solution and a filter paper spot test.

The CEC of the soils were evaluated according to the following equation:

CEC = Volume (ml) of 0.01(M) MB solution consumed/ weight of the soil sample.

All the CEC analyses were done in duplicate. For the purpose of statistical analysis/accuracy and precision of the method, CEC determination was repeated several times for two samples viz. S-17 and SS – 20 both by conventional NH_4OAc method and MB – TSPP method.

Results and Discussion

Soils were extremely acidic to moderately alkaline (pH 4.1 – 7.4), loamy sand to clay and low to high in organic carbon content (Table 1). The CEC values measured with ammonium acetate exchange were higher than the CEC measured with MB-acid and MB-H_2O filter paper spot test titration, but lower than the CEC measured with MB-TSPP titration method (Table 2). Similar finding was also reported by Wang et al. (1996). The CEC obtained by MB spot test titration method was due to exchange of the surface cation by the methylene blue ions (Maged and Ulrich 2000). In the case of MB-TSPP titration, due to high pH of TSPP solution (pH $\approx$ 10) and the dispersed reagent in the suspension, the exchange sites were completely saturated by MB. Ana et al. (2000) suggested that the cationic dye is initially rapidly adsorbed at the external surfaces, inducing the dye to form high aggregates which subsequently de-aggregate and migrate to the inter-lamellar region with time, in which they became protonated [MBH_2^+] due to presence of acidic sites. However, saturation of cation exchange sites is certainly smaller for MB-acid and MB-H_2O methods due to lower pH of the suspension. The tendency of underestimation of CEC values is more with MB-H_2O titration than with MB-acid titration. The underestimation of CEC may also be possibly due to extensive aggregation, formation of H^+ or Al clay with H_2SO_4 treatment or inhibition of MB sorption under such experimental conditions (Coleman and Harward 1953). Moreover, for the very slightly calcareous samples, the CEC value obtained through ammonium acetate method might have been underestimated. Calcium ions dissolved from $CaCO_3$ possibly inhibited complete saturation of

Table 1. Some important physical and chemical properties of soils

Site-location/Soil samples	Depth (m)	pH aq(1:2.5)	O.C. (g kg^{-1})	Sand	Silt	Clay	Tex-tural class	CaCO3 (g kg^{-1})
				---------- (%) ----------				
Village Hatikundar, Block: Hura, Dist. Puruliya, West Bengal(S-1)	0.00-0.15	5.4	6.1	59.0	16.0	25.0	scl	--
Village Ledabera, Block: Puruliya-II, Dist. Puruliya, West Bengal(S-2)	0.00-0.15	5.4	9.2	57.9	20.2	21.9	scl	--
Village Bashitanr, Block: Bagmundi, Dist. Puruliya, West Bengal(SS-3)	0.15-0.30	5.3	2.2	69.8	22.0	8.2	sl	--
Village Chatni,Block: Bagmundi, Dist. Puruliya, West Bengal (S-4)	0.00-0.15	6.3	9.3	68.8	12.2	19.0	sl	--
Village Jilinglahar, Block: Jhalda-II, Dist. Puruliya, West Bengal (SS-5)	0.15-0.30	5.2	2.1	71.7	8.2	20.1	scl	--
Village Bharatdih, Block: Kashipur, Dist. Puruliya, West Bengal (S-6)	0.00-0.15	6.8	5.2	72.6	2.5	24.9	scl	--
Farm Soil, CRRI, Block 'X', Dist. Cuttack, Orissa (SS-7)	0.15-0.30	7.4	5.5	7.0	45.4	47.6	sic	1.5
Village Bashitanr, Block: Bagmundi, Dist. Puruliya, West Bengal (S-8)	0.00-0.15	4.1	3.0	78.3	15.4	6.3	ls	--
Village Lohdungri, Block: Bagmundi, Dist. Puruliya, West Bengal (SS-9)	0.15-0.30	5.9	6.1	70.0	23.0	7.0	sl	--
Farm Soil, CRRI-Block 'B', Dist. Cuttack, Orissa (SS-10)	0.15-0.30	7.4	4.6	32.5	32.6	34.9	cl	1.1
Farm Soil, CRRI-Block 'C', Dist. Cuttack, Orissa (S-11)	0.00-0.15	7.2	1.2	84.3	7.8	7.9	ls	--
Village Lohdungri, Block: Bagmundi, Dist. Puruliya, West Bengal(S-12)	0.00-0.15	6.3	9.3	79.0	15.8	5.2	ls	--
Farm Soil, CRRI-Block 'X', Dist. Cuttack, Orissa (S-13)	0.00-0.15	6.0	9.7	13.6	52.1	34.3	sicl	--
Village Jilinglahar, Block: Jhalda-II, Dist. Puruliya, West Bengal (S-14)	0.00-0.15	5.0	3.2	82.8	5.1	12.1	ls	--
Village Ledabera, Block: Puruliya-II, Dist. Puruliya, West Bengal(SS-15)	0.15-0.30	7.4	5.1	60.9	16.9	22.2	scl	1.0
Farm Soil, CRRI-Block 'V', Dist. Cuttack, Orissa (S-16)	0.00-0.15	5.3	9.3	22.3	47.1	30.6	cl	--
Village Shalgadumdumi, Block:Arsha, Dist. Puruliya, West Bengal (S-17)	0.00-0.15	4.2	12.1	81.9	12.2	5.9	ls	--
Farm Soil, CRRI-Block 'V', Dist. Cuttack, Orissa (S-18)	0.00-0.15	6.1	6.5	45.0	38.2	16.8	l	--
Farm Soil, CRRI-Block 'V', Dist. Cuttack, Orissa (SS-19)	0.15-0.30	7.0	2.5	80.7	5.1	14.2	sl	--
Farm Soil, CRRI-Block 'V', Dist. Cuttack, Orissa (SS-20)	0.15-0.30	7.4	4.6	20.1	31.3	48.6	c	1.8

S = Surface (0.00 – 0.15 m); SS = Sub-surface (0.15 – 0.30 m)

Table 2. Cation exchange capacity of soils determined by neutral normal NH_4OA_C, MB-TSPP, MB-Acid and MB-H_2O filter paper spot test titration methods

Soil Samples	Cation exchange capacity [cmol(p^+kg^{-1}]			
	NH_4OA_C	MB-TSPP	MB-Acid	MB-H_2O
S1	10.4	13.0	11.4	6.7
S2	8.6	9.2	10.1	6.0
SS3	3.6	5.4	6.2	4.2
S4	8.8	9.0	5.4	4.4
SS5	8.6	8.2	5.3	4.6
S6	7.5	8.4	5.1	5.0
SS7	22.6	22.2	12.8	12.2
S8	3.2	4.8	5.0	5.8
SS9	6.0	6.8	4.9	4.8
SS10	16.1	16.6	7.2	9.6
S11	4.0	4.8	3.9	3.6
S12	4.5	5.2	2.5	3.5
S13	17.4	19.2	14.6	9.2
S14	5.2	6.2	4.6	4.2
SS15	8.4	9.2	6.8	8.2
S16	14.3	17.0	11.2	8.8
S17	7.0	7.8	3.5	3.4
S18	8.9	9.6	6.8	5.2
SS19	6.6	7.2	4.8	4.4
SS20	25.5	30.8	15.6	11.8
*Average error(%)	-	15.6	31.8	35.9

*Average error(%) [∑(| CEC_{NH4OAc} - $CEC_{MB-TSPP}$ |) x 100 / CEC_{NH4OAc})]/n
where n = no. of observations

exchange sites with NH_4^+ ions, thereby resulting in low CEC values.

The MB-TSPP against ammonium acetate CEC shows a small average error (15.6%) compared to 31.8% and 35.9% for MB-acid and MB-H_2O titration, respectively (Table 2). Average error of 16.8%, 21.6% and 21.3% for MB-TSPP, MB-acid and MB-H_2O filter paper spot test titration, respectively against ammonium acetate method was reported by Wang et al. (1996).

Correlation analysis indicated positive and highly significant correlation for MB-TSPP with ammonium acetate method (r = 0.986; significant at 1% level) and yielded simple regression equation viz.

$(CEC)_{NH4OAc}$ = 0.897 $(CEC)_{MB-TSPP}$ − 0.035, for routine conversion for agricultural soils under Indian conditions.

Step-wise multiple regression analysis was carried out relating clay and organic matter to soil CEC (Table 3). A drop in variation from 92% to 91% and 88% to 87%, respectively was observed for both the methods (NH_4OAc and MB – TSPP) when step down regression analysis was done to exclude the effect of organic matter upon CEC. However, a drastic fall in the overall variation from 92% to 3% and 88% to 3%, respectively was observed while excluding clay factor in step-down regression suggesting the importance of the latter in the process of cation exchange. Statistical analysis for paired

Table 3. Stepwise multiple regression equation relating clay and organic matter to cation exchange capacity

Equation No.	Multiple Regression Equations	R^2
1.	$CEC_{(NH4OAc)} = 0.45 \, (Clay) + 0.13 \, (OM) - 0.61$	0.92
2.	$CEC_{(NH4OAc)} = 0.45 \, (Clay) + 0.59$	0.91
3.	$CEC_{(NH4OAc)} = 0.21 \, (OM) + 7.74$	0.03
4.	$CEC_{(MB \, TSPP)} = 0.48 \, (Clay) + 0.13 \, (OM) - 0.10$	0.88
5.	$CEC_{(MB \, TSPP)} = 0.48 \, (Clay) + 0.09$	0.87
6.	$CEC_{(MB \, TSPP)} = 0.21 \, (OM) + 8.87$	0.03

OM = Organic matter

observation test of significance (t) and F-Test for sample variance revealed that the mean values of CEC of soils estimated by both the methods did not vary significantly at 5% level.

Conclusion

The MB-TSPP filter paper spot test may be recommended for rapid CEC determination of soils in field as it is simple and less time consuming. The method needs to be validated in different classes of soils, before it could become an universally accepted method.

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