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Methylene Blue Spot Test for Cation Exchange Capacity (CEC) Estimation in Acid Soils of India

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Abstract

In order to establish a simple, rapid and cost effective method of estimating cation exchange capacity (CEC) of acidic soils, we tested the utility of methylene blue spot test (MBST) *vis-à-vis* commonly used neutral 1*N* ammonium acetate method (NAAM) in twenty acidic soils. The soils collected from ten different states of India varied widely in pH, organic carbon content and texture. Averaged across the soils, MBST-CEC was 37% lower than the NAAM-CEC, due possibly to the differences in pH at which the two methods operate. The CEC values estimated by MBST correlated strongly (R=0.89) with those obtained by NAAM, implying that MBST can be used satisfactorily to measure CEC of acidic soils. An equation for inter-conversion of CEC values obtained by the two methods was also worked out. Since NAAM is a time taking and tedious procedure, we recommend MBST method for routine estimation of CEC in acidic soils of India. The method is easily applicable with simple test equipments including filter papers, a glass rod or dropper and methylene blue dye. More than 60 samples a day can easily be analyzed for CEC using MBST method. Being a simple, rapid and cost effective method, the MBST can be included in rapid soil testing kits. Given the importance of CEC in soil fertility and plant nutrition, MBST-CEC may also be included in the soil health cards distributed to the farmers.

1. Introduction

Cation exchange capacity (CEC) is an important property of soil governing soil fertility and plant nutrition. It is the capacity of the soil to hold and exchange cations. Importance of cation exchange phenomenon in soil can be understood given that the ion exchange has long been regarded as the most important chemical reaction on earth after photosynthesis (Meetei *et al.*, 2020). Cation exchange provides a buffering effect to changes in soil pH and available nutrients. It is a major controlling agent of stability of soil structure, nutrient availability for plant growth, soil pH, and the soil's reaction to fertilizers and other ameliorants. A low CEC means the soil has a low resistance to changes in soil chemistry that are caused by land use (Hazleton and Murphy, 2007). Soils have a CEC primarily because clay particles and organic matter in the soil tends to be negatively charged.

Cation exchange capacity is usually estimated by displacing the exchangeable cations with another strongly adsorbed cation, and then determining how much of the strongly adsorbed cation is retained by the soil. The strongly adsorbed cation can be supplied by reagents such as ammonium chloride, ammonium acetate, silver thiourea, barium chloride and potassium chloride (Rengasamy and Churchman, 1999). In India, neutral 1*N* ammonium acetate ($NH_4C_2H_3O_2$) is commonly used to determine the CEC of soils across the pH values ranging from very low to very high. Considering the importance of CEC as a master soil property, its inclusion in rapid soil testing kits and in soil health cards would be worthwhile. The commonly used 'ammonium acetate method', however, is not 'simple and rapid enough' to be included in rapid soil testing kits. A more rapid, simple and cost effective method would serve the purpose better. Methylene blue in aqueous solution is a cationic dye, $C_{16}H_{18}N_3S^+$, which bonds to negatively charged

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surfaces of soils (Hang and Brindley, 1970; Chen *et al*., 1999). The bond is strong enough to displace almost all of the exchangeable cations bound on soil particles. The amount that bonds can be taken as a measure of soil CEC. The method, though very simple and rapid, has never been tested for CEC determination in Indian soils. The objective of our study was therefore to examine the utility of the simplest version of the methylene blue method *i.e.* methylene blue spot test (MBST) for CEC estimation in acidic soils of India.

2. Materials and Methods

A total of twenty (20) acidic soils collected from ten different states of India (two each from Meghalaya, Manipur, Mizoram, Arunachal Pradesh, Tripura, Nagaland, Assam, West Bengal, Jharkhand and Karnataka) were used for this study. The soils varied widely in basic properties including pH (4.10-6.97), texture (sandy loam – clay loam) and organic carbon (0.4-2.7%) content. Cation exchange capacity (CEC) of all the soils was determined using the conventional 'neutral 1*N* ammonium acetate (NH_4OAc) method' (NAAM) (Schollenberger and Simon, 1945), and also by methylene blue spot test (MBST) (Kandhal and Parker, 1998; Santamarina *et al*., 2002; Yukselen and Kaya, 2008). The chemical formula of methylene blue (MB) is $C_{16}H_{18}ClN_3S$, with a corresponding molecular weight of 319.87 g mol^{-1}. Its IUPAC name is: [7-(dimethylamino) phenothiazin-3-ylidene]-dimethylazanium chloride. Chemical structure of MB is shown in Figure 1 (PubChem, 2021).

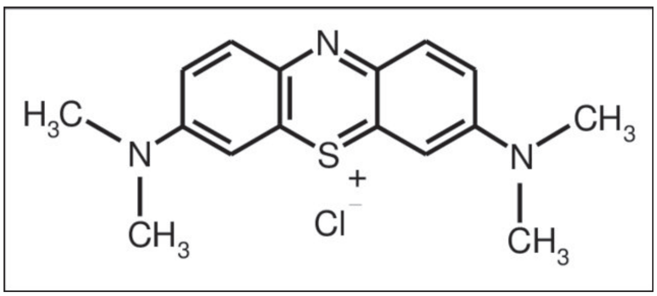

Figure 1: Chemical structure of Methylene Blue

The spot test procedure for determining the CEC of soils (Santamarina *et al*., 2002) was slightly modified to suit the local requirement, keeping in view the relatively lower CEC values of the Indian soils. Briefly, methylene blue solution was prepared by mixing 1 g dry powder of MB with 250 mL of deionized water. Ten grams of soil was mixed with 30 mL deionized water. Then, the MB solution was added into this soil suspension with 0.5 mL increments. After each 0.5 mL addition of MB, soil suspension was mixed and stirred for 1 min by a glass rod; then, a small drop was removed from the solution and placed onto the filter paper. Initially, added MB was totally adsorbed by the soil leaving no blue halo around the aggregate spot on the filter paper. With further increments of the MB solution, there came a point when the unadsorbed MB formed a permanent light blue halo around the aggregate spot on the filter paper (spots with no MB halo and spot with blue MB halo look like as shown in Figure 2), CEC was determined using the following formula (Cokca and Birand, 1993).

$$CEC = \frac{100}{W_S} \times V_{mb} \times N_{mb}$$

Where, CEC = the cation exchange capacity (meq 100 g^{-1} soil), W_S = weight of the soil sample (g), V_{mb} = volume of the MB solution consumed (mL), and N_{mb} = normality of the MB solution (meq mL^{-1}).

$$N_{mb} = \frac{\text{Weight of methylene blue(g)}}{320} \times \frac{100\text{-}X}{100}$$

Where, X = the moisture content (%) of the MB substance.

For better precision, CEC of each soil sample was tested twice by both the methods (NAAM and MBST), and the average of the two values for each sample obtained by both the methods were tested for the strength of correlation.

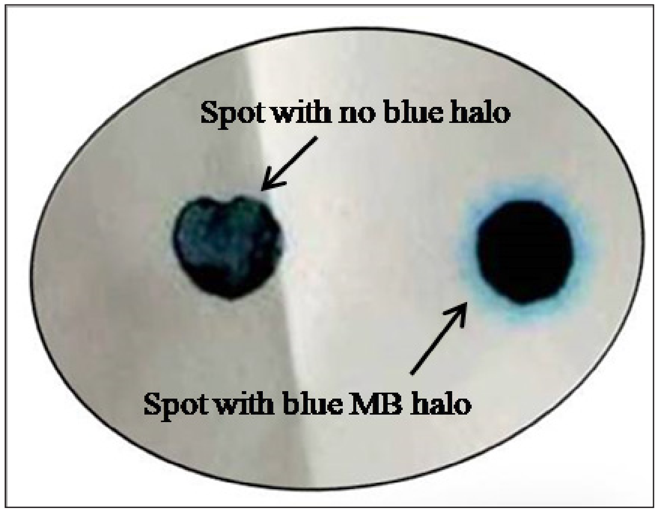

Figure 2: Representation of the spots (with and without MB halo) on filter paper as found in MB spot test for a soil's CEC estimation

3. Results and Discussion

Cation exchange capacity of the soils determined by neutral 1*N* ammonium acetate method (NAAM) and by methylene blue spot test (MBST) ranged from 2.9 to 11.0 and 1.2 to 7.8 meq 100 g^{-1}, respectively. Across the soils, the NAAM based CEC values were higher than those obtained by MBST (Figure 3). On average, MBST-CEC values were 37% lower than the NAAM-CEC. Lower values of MBST-CEC *vis-à-vis* NAAM-CEC were also reported by Milosevic *et al*. (2015) and Yukselen and Kaya (2008). According to Milosevic *et al*. (2015), main difference between the two tests is due to molecular aggregation of MB on the clay surface. NAAM method is highly sensitive to the presence of CaO. Release of Ca ion from the sample into the solution can limit the saturation of exchange sites by the ammonium ion. Taylor (1985), Soon (1988), and Wang *et al*. (1996) also reported higher CEC values of clayey soils measured with NH_4-Na exchange than those measured with MB method. According to Coleman and Harward (1953),

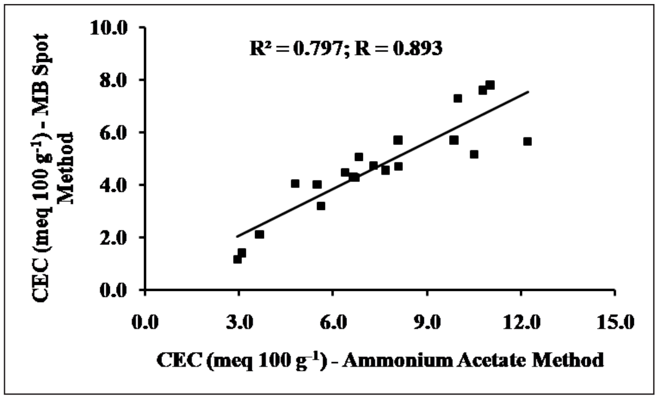

Figure 3: Correlation between CEC values obtained by methylene blue spot test and ammonium acetate method

the difference between the two CEC determination methods is possibly caused by extensive aggregation, formation of H^+, or inhibition of MB sorption. In addition, higher CEC values by NAAM method may also be due to the CEC measurement at neutral pH (7.0) in this method, while MBST method measured CEC at lower soil pH (close to natural soil pH) in acid soils used for our study. As negative charge increases at high pH, CEC measured at higher pH would naturally be higher than its measurement at natural pH (lower pH) in acid soils. Edmeades (1982) while studying the effect of lime on the effective cation exchange capacity (ECEC) of the New Zealand soils reported higher ECEC in all the soils at higher pH caused by liming. We therefore envisage that MBST-CEC values may be closer to the ECEC values (measured at natural soil pH) than to NAAM-CEC values of acid soils. Confirmatory studies are required in this direction.

Though there were differences in the absolute values of CEC measured by both the methods, strong correlation (R=0.89) was observed between the CEC values obtained by MBST and NAAM methods (Figure 3), which implies that MBST can be used effectively to measure the CEC of acid soils in India. Almost similar correlation coefficient (0.88) between the MBST-CEC and NH_4-Na results was reported by Yukselen and Kaya (2008). Wang *et al*. (1996) had also previously reported a correlation coefficient of 0.86 between CEC values determined by ammonium acetate method and MB titration method. For reporting of MBST-CEC values in terms of NAAM-CEC, we also developed an equation for inter-conversion of both the values.

$$\text{CEC (NAAM)} = \frac{[\text{CEC (MBST)} - 0.26]}{0.59}$$

Where, CEC (NAAM) is the CEC (meq 100 g^{-1} soil) obtained with neutral 1*N* ammonium acetate method and CEC (MBST) is the CEC (meq 100 g^{-1} soil) obtained from methylene blue spot test.

Results of our study, corroborated strongly by many previous studies, give enough reason and confidence for adoption of methylene blue drop test for CEC estimation in routine soil testing in India. Since the method is very simple, rapid and cost effective, MBST can be included in rapid soil test kits and the values may also be reported in soil health cards distributed to the farmers across the nation.

Our results hold particular significance for acid soils which covers nearly one-third of the cultivated land in India, and over 95% of the land area in northeastern region of the country (Sharma and Singh, 2002; Kumar *et al*., 2021b). Liming is a commonly advocated practice to ameliorate acid soils for improving crop production (Kumar *et al*., 2012a,b; Singh *et al*., 2014; Kumar *et al*., 2016 & 2021a). And the required dose of liming (lime requirement, LR) depends largely on soil organic carbon and clay content, besides soil pH, as they are the most important determinants of soil's buffering capacity (Sims, 1996; Kumar *et al*., 2012b). They also happen to be the three most important variables regulating the soil's CEC, implying that lime requirement of acid soils must be greatly influenced by their CEC. Therefore, a rapid method of estimating lime requirement based on soil's CEC and pH may also be worked out. Rapid test facility for soil pH is already available in most soil test kits, and If MBST method is used for estimation of soil CEC, the two values can possibly combine to give a rapid and automated estimation of lime requirement. Since CEC is a master soil property, its rapid estimation can be used to generate many more information related to soil fertility, nutrient management and soil ameliorations. Utility of MB spot test as well as titration method for CEC estimation in Indian soils, particularly with higher pH and varying physico-chemical properties merits further investigation.

4. Conclusion

Cation exchange capacity of the twenty acidic soils, varying widely in pH, organic carbon and texture, estimated by methylene blue spot test (MBST) correlated strongly (R=0.89) with the CEC values obtained by commonly used neutral 1*N* ammonium acetate method (NAAM). Since NAAM is a time taking and tedious procedure, we recommend MBST method for routine estimation of CEC in acidic soils of India. Being a simple, rapid and cost effective method, MBST can be included in rapid soil testing kits. Given the importance of CEC in soil fertility and plant nutrition, MBST-CEC may also be included in the soil health cards distributed to the farmers under the "Soil Health Card Scheme".

5. Acknowledgement

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