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Suitability of the methylene blue test for surface area, cation exchange capacity and swell potential determination of clayey soils

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ABSTRACT

Application of the methylene blue test methods in determining soil properties, including specific surface area (SSA), cation exchange capacity (CEC), swell index, and swell potential are investigated on clayey soil samples with widely different mineralogy. The results indicate that the MB methods yield accurate prediction of some soil index properties, and they are easy to apply with simple test equipment. The results also show that the testing methods can be applied for soils that have widely different mineralogy. External and internal surface areas of soils can be measured by the MB adsorption methods. Effect of particle size on the MB surface area measurement accuracy was also studied using samples passing 0.425 mm (No. 40) and 0.075 mm (No. 200) sieves. The results show that there is no significant difference in the amount of absorbed methylene blue of the soil samples passing the No. 40 and No. 200 sieves. The test results also indicate that the MB-CEC values are generally lower than those obtained by the ammonium acetate method. The correlation coefficient between the MB-CEC and NH_4-Na results is 0.88 indicating that MB can be used effectively to measure CEC of soils. The results also show that swell index and swell potential of the soils can be estimated with MB methods accurately, economically and readily. Significant relationship is observed between the swelling potential and MBV (methylene blue value) for a wide range of soils. A new classification for swelling soils is proposed using MBV.

1. Introduction

Methylene blue (MB) test has become popular because they are easily applicable and need no special equipment; yet, they yield accurate results. Readily available soil index properties obtained using MB method become important especially for preliminary site investigations. To this end, the MB test methods were used for determining cation exchange capacity (Nevins and Weintritt, 1967; Taylor, 1985; Kahr and Madsen, 1995), specific surface area (Phelps and Harris, 1968; Santamarina et al., 2002; Chiappone et al., 2004; Yukselen and Kaya, 2006), swell potential (Fityus et al., 2000; Meisina, 2000; Erguler and Ulusay, 2003a; Avsar et al., 2005), fine fraction determination in loose material (Pantet et al., 2007) and in concrete or mortar (Yool et al., 1998), etc.

Surface area measurements of clayey soils are important for characterizing their dry bonding power, plasticity, flow properties, adsorbing polar compounds such as some pesticides and pollutants and for swell-shrinkage behavior. However, specific surface area of clayey soils shows great variation depending on their mineralogy, organic composition, and particle size dimensions. Thus, several methods, derived from different physico-chemical point of views have been developed to measure specific surface area of clayey soils. Some of these methods are adsorption of nitrogen (N_2) (Brunauer et al., 1938) or water vapor (Newman, 1983), ethylene glycol (EG) and ethylene glycol monoethly ether (EGME) (Churchman et al., 1991; Cerato and Lutenegger, 2002), methylene blue (Kipling and Wilson, 1960; Hang and Brindley, 1970; Tran Ngoc Lan, 1979; Kahr and Madsen, 1995; Chen et al., 1999; Santamarina et al., 2002), *p*-Nitrophenol (Ristori et al., 1989), polyvinylalcohol (Pagel-Wieder and Fischer, 2001), poly (ethylene oxide) and non-ionic surfactant. Some of these methods are either time consuming or they require elaborate, delicate and expensive equipment. Hence, a simple method that would yield reliable results is needed.

Methylene blue dye has been used for determining SSA of various materials for several decades. Methylene blue in aqueous state is a cationic dye, $C_{16}H_{18}N_3S^+$, which can adsorb onto negatively charged clay surfaces. The MB molecule has a rectangular shape with dimensions 17 Å*7.6 Å*3.25 Å, and it is assumed that MB molecule lies on its largest surface. The surface area covered by one MB molecule is assumed to be approximately 130 $Å^2$ (Santamarina et al., 2002). Santamarina et al. (2002) compared N_2 and MB adsorption methods for surface area

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measurements. They observed that N_2 adsorption method renders low values of SSA in swelling clays since N_2 molecules cannot penetrate into inner layers. The N_2 adsorption method yields only external surface; however, MB method can yield total (external + internal) surface area of soils.

Further, cation exchange capacity (CEC) of soils is needed for many geotechnical applications. However, standard methods of CEC determination are time consuming and involve several steps (e.g., displacement of the saturating cation requires several washings with alcohol). Thus, researchers sought for a method that can be easily applicable; yet, yield accurate results. Realizing that dye adsorption onto clay surfaces occurs by two mechanisms: (i) cation exchange in the alumino-silicate lattice, and (ii) attraction of van der Waals forces or chemisorption (hydrogen bonding) with the surface SiOH and AlOH of the alumino-silicate lattice, researchers (Nevins and Weintritt 1967; Çokca and Birand, 1993b) determined CEC of soils by measuring adsorption of MB from aqueous solutions onto clay surfaces. Several successful application of MB adsorption method to determine CEC of clayey soils can be found in the literature (Çokca and Birand, 1993b; Wang et al., 1996 etc).

Expansive soils may result in considerable distress when subjected to moisture variations due to seasonal climatic conditions. Consequently, severe damage to overlying light structures and related problems has been reported in many countries (Popescu, 1979; Erguler and Ulusay, 2003b). Numerous reports relating expansive soil damages to superstructures led researchers to develop predictive equations for estimating the swelling pressure and swelling percentage of expansive clays from geotechnical index properties (Sivapullaiah et al., 2000; Erguler and Ulusay, 2003a; Avsar et al., 2005). However, the developed predictive equations are mostly regional dependent and cannot be generalized. Thus, researchers sought alternative methods to estimate the swelling potential of soils. For example, Erguler and Ulusay (2003a) observed that methylene blue value (MBV) is a good predictor for swelling pressure and swelling percentage. Further, Fityus et al. (2000) found that by adopting a streamlined titration technique, MBVs can be obtained quickly and reliably with the preparation time for the MB test being similar to the shrink–swell test. Unlike the shrink–swell test, however, it has the major advantage of yielding immediate results.

In the present study, the relevance of two MB methods, namely MB-titration and MB-spot test, to measure specific surface area, cation exchange capacity, and swell potential of the soils having with wide range of mineralogy was investigated. Hereby, the relationship between the soil index properties and the MB values were also studied.

2. Materials and methods

In this study, sixteen different soils of varying origins and characteristics were selected. All samples were obtained from different regions of Turkey, except Soil-4, which is a Georgia kaolinite (KGa1-b) obtained from Source Clays Repository–Purdue University. X-Ray powder diffraction patterns were obtained using a Philips diffractometer and CuKα radiation. Dominant mineral of the soils and the clay fractions of the samples are given in Table 1. All soil samples were oven-dried (80 °C–48 h), crushed and sieved. Grain size distribution, specific gravity, cation exchange capacity and organic matter content (OM) of the samples were determined according to ASTM D-422-63 (1999), ASTM D-854-92 (1999), and Na method (Chapman, 1965), ASTM D-2974-87 (1999), respectively. Liquid, plastic, and shrinkage limits were determined according to British Standards (BSI, 1990), ASTM D-4318-98 (1999), and ASTM D-427-93 (1999), respectively. The results of these tests are given in Table 1.

Specific surface area of the samples was determined with two MB (spot and titration) and N_2 adsorption methods. All tests were run twice for the accuracy of the results. Based on the literature (Zohar et al., 1983; Jong, 1999), the soils were oven-dried and no treatment were applied to the soils.

2.1. N_2 adsorption method

The BET-N_2 specific surface area was determined by nitrogen adsorption test by using a Quantachrome Monosorb® device. Before testing, the samples were out gassed and dried at 77 K in the heating mantle of the device. The theoretical basis upon which the Monosorb operates is the BET equation (Brunauer et al., 1938). The device was calibrated by injection of 1 cm^3 nitrogen gas. The measured area was 2.84 ± 0.3 m^2g^{-1} (1 cm^3 N_2 has 2.84 m^2g^{-1} specific surface area) during the test.

2.2. Methylene blue — spot test method

The spot test procedure for determining the SSA of soils is described as follows (Santamarina et al., 2002): Methylene blue solution was prepared by mixing 1 g dry powder of MB with 200 mL of deionized water. Ten grams of oven-dried 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 by magnetic stirrer for 1 min; then, a small drop was removed from the solution and placed onto Fisher brand filter paper. If the unadsorbed MB forms a permanent blue halo

Table 1
Characteristics of the soils

Sample #	Clay Fraction (<2 μm)	Specific Gravity	LL (%)	PI	SL (%)	Organic matter content (OM) (%)	Activity PI/CF	Location	Dominant Mineral*
S-1	32.5	2.50	58.0	14.1	38.8	10.4	0.43	Çanakkale	K
S-2	44	2.63	30.1	–	20.4	2.3	–	Balıkesir	K
S-3	38	2.52	51.7	9.8	34.8	1.9	0.26	İzmir	K
S-4	42	2.63	42.0	16.0	26.0	2.7	0.53	Georgia, USA	K
S-5	28	2.48	58.4	23.3	27.9	10.5	0.83	Bozhöyük	H
S-6	35.5	2.39	61.6	11.4	39.3	5.6	0.32	Gördes	Z
S-7	32	2.36	44.9	6.2	35.9	4.8	0.19	Bigadiç	Z
S-8	21	2.75	24.5	6.5	16.1	1.8	0.31	Manisa	C
S-9	77	2.76	72.2	37.5	17.3	4.4	0.49	Çanakkale	MMC
S-10	46	2.63	60.9	43.2	16.8	1.5	0.94	Ordu	I
S-11	82	2.50	113.6	52.9	19.8	7.0	0.65	Bozhöyük	M
S-12	75	2.64	70.0	40.2	16.8	5.2	0.54	İstanbul	M
S-13	90	2.76	464.8	416.6	10.4	2.4	4.63	İstanbul	M
S-14	56.8	2.37	111.5	69.9	5.8	5.0	1.23	Balıkesir	M
S-15	80	2.76	330.7	280.8	7.1	2.2	3.51	Balıkesir	M
S-16	90	2.72	395.8	343.4	11.7	2.3	3.82	Balıkesir	M

*K:Kaolinite, H:Halloysite, Z:Zeolite, C:Chlorite, MMC:Mixed mineral clay, I:Illite, M:montmorillonite.

around the soil aggregate spot onto the filter paper, it means that MB has replaced cations in the double layer and coated the entire surface. Surface area is determined from the MB amount that required reaching the end- point from the following equation:

$$\mathrm{SSA} = \frac{1}{319.87}\frac{1}{200}(0.5N)A_{\mathrm{v}}A_{\mathrm{MB}}\frac{1}{10} \tag{1}$$

where N is the number of MB increments added to the soil suspension solution, A_{v} is Avogadro's number ($6.02*10^{23}$/mol), and A_{MB} is the area covered by one MB molecule (typically assumed to be 130 Å^2). For practical purposes, it is sufficient to dry the dye at 105 °C to constant weight in order to attain anhydrous state of MB.

2.3. Methylene blue — titration method

In this method, a spectrophotometer is used to determine the amount of MB remaining in the solution. Spectrophotometer improves the accuracy of determining the adsorbed MB. The test procedure is described as follows (Santamarina et al., 2002): Two grams of oven-dried specimen was mixed with 200 mL of deionized water in a 500 mL flask. The MB solution was added to soil suspension (the concentration is the same as that was used in the spot test). The suspension was mixed continually for about 2 h with shaker, and allowed to sit overnight to reach adsorption equilibrium and allow particle settlement. Then 5 mL of the fluid was removed, and then it is centrifuged. The remnant concentration of MB in the fluid was determined by NovaSpec II spectrophotometer, at wavelength of 655 nm. The value of specific surface was derived from the point of complete cation replacement determined on the titration curve. When the curve deviates from 45° line, it means that added MB cannot be adsorbed by the soil completely. In other words, all the exchange sites of the soil are covered by MB molecules. At this optimum point, the SSA is computed from the amount of adsorbed MB by the following equation:

$$\mathrm{SSA} = \frac{m_{\mathrm{MB}}}{319.87}A_{\mathrm{v}}A_{\mathrm{MB}}\frac{1}{m_{\mathrm{s}}} \tag{2}$$

where m_{MB} is the mass of the adsorbed MB at the point of complete cation replacement, and m_{s} is the mass of the soil specimen.

3. Cation exchange capacity

As indicated above, CEC of soils can be determined by MB methods. The assumption is that the MB dye is capable of attaching itself to the exchange sites on the mineral surface by replacing the exchangeable cations. Plotting the adsorbed MB against the added MB shows a deviation from the 45° straight line (Fig. 1) in the titration method. In the spot test, the optimum flocculation point is attained when the unadsorbed MB formed a permanent light blue halo around the aggregate spot on the filter paper. At this point, CEC is determined by the following the formula (Çokca and Birand, 1993b):

$$C = \frac{100}{m_{\mathrm{S}}}V_{\mathrm{cc}}N_{\mathrm{mb}} \tag{3}$$

where C = the cation exchange (meq/100 g clay), m_{S} = weight of the specimen, g, V_{cc} = the volume of the MB titrant, mL, and N_{mb} = the normality of the MB substance, meq/mL.

$$N_{\mathrm{mb}} = \frac{\text{weight of methylene blue (g)}}{320}\frac{100-X}{100} \tag{4}$$

where X = the moisture content of the MB substance, %.

4. Swell index

The swell index of the samples was determined using oedometer test (ASTM D-2435) and the combination of ASTM D-5890 and Sivapullaiah et al. (1987) methods. In the oedometer test, the soil samples were prepared at their liquid limits and loaded axially with total stress increments (12.3, 24.5, 49, 98.1, 196.1, 392.3, and 784.5 kPa). Each stress

Table 2
Specific surface area of the soils by N_2 adsorption, MB-titration and MB-spot test methods

Specific surface area ($m^2\ g^{-1}$)			
Sample #	N_2	MB-titration	MB-Spot Test
S-1	56.4	48.9	57.6
S-2	6.9	6.1	14.4
S-3	20.8	12.2	26.4
S-4	10.1	12.2	21.6
S-5	93.5	61.0	79.2
S-6	34.3	122.1	136.8
S-7	32.0	47.1	54.0
S-8	5.3	18.3	26.4
S-9	25.3	84.9	106.8
S-10	15.5	73.4	100.8
S-11	56.7	244.1	364.8
S-12	36.4	158.3	168.0
S-13	51.9	850.9	720.0
S-14	11.2	704.6	753.6
S-15	28.7	777.5	768.0
S-16	21.5	948.8	912.0

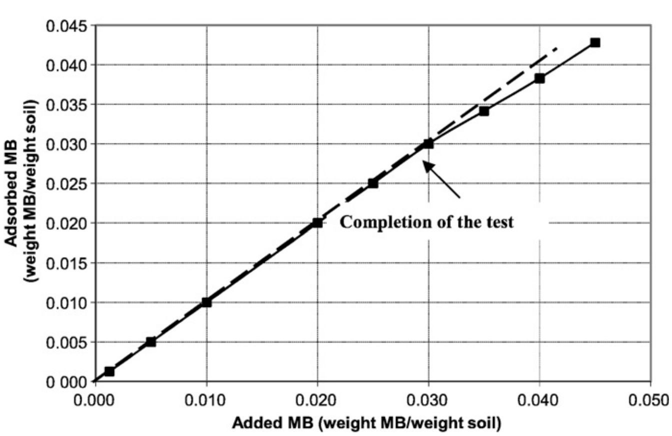

Fig. 1. The determination of the point of complete replacement of cations from the titration curve (Sample 9).

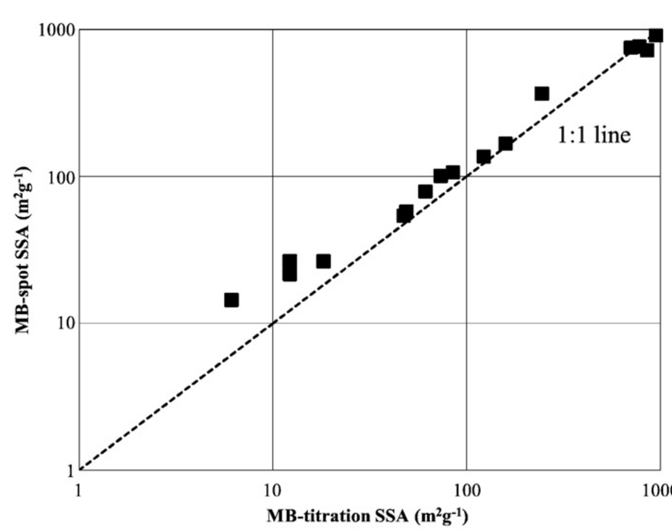

Fig. 2. Relationships between the MB methods.

Table 3
Adsorbed MB values of No.200, No. 40, and No.40 passing Na-exchanged samples

Adsorbed MB-spot test (mL)			
Sample #	No. 200 passing (0.075 mm)	No. 40 passing (0.425 mm)	No. 40 passing-Na exchanged
S-1	48	46	40
S-2	12	8	8
S-3	22	18	24
S-4	18	17	24
S-5	66	50	30
S-6	114	105	76
S-7	45	30	28
S-8	22	11	10
S-9	89	89	102
S-10	84	62	82
S-11	340	340	424
S-12	140	132	130
S-13	590	580	–
S-14	628	576	640
S-15	630	632	560
S-16	748	748	705

increment was maintained until excess pore water pressure was completely dissipated. When the last stress increment was completed, the soil specimens were unloaded to 196.1, 49, and 12.3 kPa, respectively. Deformation readings were recorded until swelling process completed. Some specimens completed their swelling within 24 h; however, some specimens swelling process continued up to 28 days. The samples were prepared at their liquid limits as “swelling” properties are inherent to the soil and independent of the natural state (fabric, bounding, etc.) (Burland, 1990; Cerato and Lutenegger, 2004).

Swell index of samples with accordance ASTM D-5890 was determined in terms of mL/2 g. In this adapted swell index method, oven-dried and passed through No. 40 (0.425 mm) sieve of 10 g of non-swelling soils and oven-dried and 2 g swelling soils were used. Then, 90 mL distilled water was transferred to a 100 mL graduated cylinder. Approximately 0.1 g increments of soil were dusted over the entire water surface in the graduated cylinder over a period of approximately 20 s. Soil hydration and settlement were allowed for a minimum period of 5 min. After the final increment had settled, the water volume was raised to 100 mL by rinsing the adhering particles from the sides of the cylinder. After 2 h, the hydrating clay column was inspected for trapped air. After 24 h hydration period, the volume in milliliters was recorded at the top of the settled soil. Swell index was determined as mL/2 g.

In order to observe the sodium (Na^+) saturation effect on CEC determination with MB methods, Na-exchanged samples were prepared by washing soils with NaCl (from Merck chemical) solution. The washing process was as follows: As-received soil was prepared by mixing 2 M NaCl solution for 15 min at a solid to liquid ratio of 1:2, diluted with distilled water of 2 to 3% solids. Then, it was allowed to settle, and the supernatant was discarded. The electrical conductivity was measured until negligible changes occurred. The electrical conductivity of the supernatant was decreased below 100 μmhoms by several washings with distilled water in order to wash out free salt ions. The washed soil dried at 80 °C for over 48 h.

Table 4
CEC of the samples by NH_4-Na and MB-spot test methods

CEC (meq/100 g)			
Sample #	NH_4-Na	MB-spot test	MB-Spot Test*
S-1	25.1	7.5	6.3
S-2	2.9	1.9	1.3
S-3	6.8	3.4	3.8
S-4	2.0	2.8	3.8
S-5	24.0	10.3	4.7
S-6	60.5	17.8	11.9
S-7	57.2	7.0	4.4
S-8	5.9	3.4	1.6
S-9	26.2	13.9	15.9
S-10	10.7	13.1	12.8
S-11	83.7	47.5	66.3
S-12	38.4	21.9	20.3
S-13	86.1	92.2	–
S-14	132.3	98.1	100
S-15	67.1	98.4	87.5
S-16	127.9	116.8	110.2

*Samples are in Na-exchanged form.

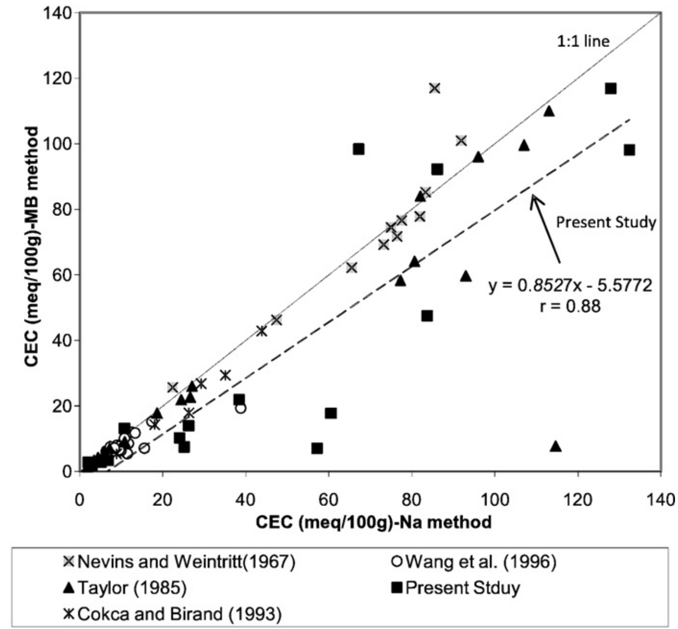

Fig. 3. Comparison of NH_4-Na and MB-spot test method for the CEC determination along with the data from literature.

5. Results and discussions

5.1. Specific surface area

The obtained SSAs of soils using two MB (titration and spot) and N_2 adsorption methods are given in Table 2. The specific surface was derived at complete cation replacement phase by titration method. The results are shown in Fig. 1 (for Soil-9). At this point, from the amount of adsorbed MB, SSA was calculated using Eq. (2).

As seen from Table 2, except Sample #5, the specific surface area measured by N_2 adsorption method are lower than those measured by

Table 5
Swell index of the samples by two different swell index methods

Sample #	Swell index (C_s)	Swell index (mL/2 g)
S-1	0.027	3.0
S-2	0.017	1.9
S-3	0.028	3.3
S-4	0.043	3.0
S-5	0.020	2.3
S-6	0.020	2.8
S-7	0.017	2.6
S-8	0.025	1.7
S-9	0.149	3.3
S-10	0.183	3.4
S-11	0.174	7.2
S-12	0.14	3.6
S-13	N/A	44.5
S-14	0.125	6.0
S-15	1.566	18.0
S-16	3.548	40.2

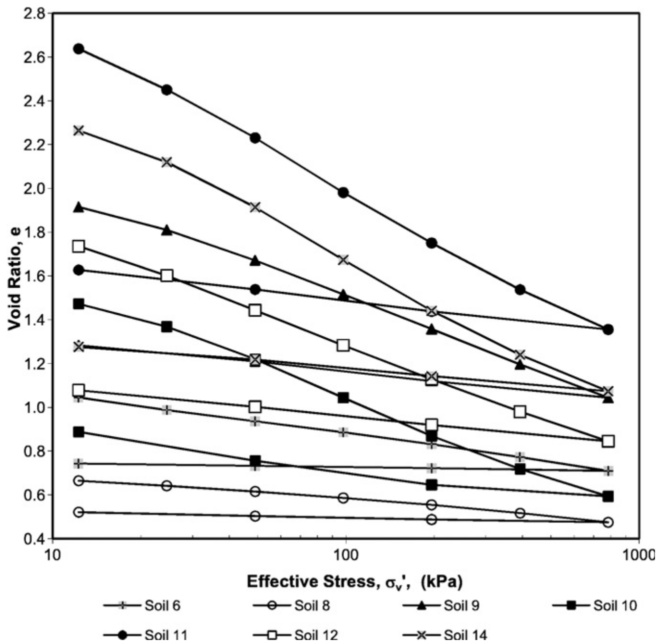

Fig. 4. Void ratio (e) — effective consolidation stress ($\bar{\sigma}_v$) diagram of the some samples.

the MB methods as N_2 method measures only the external surfaces of the soils. This difference in the measured surface areas is most pronounced for montmorillonitic soils (Samples 11 to 16) as expected. Montmorillonite mineral is composed of two silica sheets and one alumina (gibbsite) sheet. The silica sheets of adjacent clay units are held together only by weak van der Waals' bonding. Therefore, water and exchangeable ions can easily enter and separate these layers. Gas adsorption method is applied onto dry specimens under dry conditions where the montmorillonite layer is tightly bound. Thus, the molecules of selected gas (in the present study N_2 gas) cannot cover the interlayer surface in expansive layer-silicates such as montmorillonite. For this reason, the measured specific surface areas with N_2 method are only external surface areas of these soils. The methylene blue methods are applied under wet conditions in which ions or water intercalate into inner montmorillonite layers, thus MB methods measure external and internal surface area (Santamarina et al., 2002; Yukselen and Kaya, 2006). Theng et al. (1999) observed that polar and cationic organic compounds intercalate into expanding layer silicates. Such findings lead us to conclude that the MB methods should enable one to measure the area between the layers of such minerals. Further, such a conclusion is realized in Table 2. The results reveal that there is no significant difference in SSA determined using either dry or wet measurement procedures for kaolinitic soils (Table 2). However, the SSAs determined under dry conditions are lower than wet conditions for minerals such as zeolite, chlorite, mixed layer, and illite.

Two MB methods, titration and spot test yield similar SSA values. Note that generally spot test yields higher SSA estimates than the titration method. When the titration and spot test results are compared, a high coefficient of correlation is realized (r=0.99) (Fig. 2). This should be expected as these methods use the same cationic compound. In the titration method, the accuracy of the test is improved by using a spectrophotometer, which determines the remnant concentration of the MB more accurately. On the other hand, spot test contains operator-related errors such as judging the end-point. The results of titration methods are smaller than those of the spot test (Table 2). Thus, the differences between the results of two similar methods can be attributed to operator-induced errors in the spot test results.

In order to determine the effect of particle size on the MB surface area measurements, surface area of the soils passing 0.425 mm (No. 40) and 0.075 mm (No.200) were determined with spot test. The results show that there is no significant difference between the measured SSA of soils passing No. 40 and No.200 soils (Table 3). However, Hills and Pettifer (1985) reported that the particle size affects the MB determined SSA. Thus, we suggest soils passing No.40 sieve (425 μm) should be used to eliminate possible particle size effect and maintain uniformity of the test results, even though no particle size effect is determined in this study.

Chen et al. (1999) observed the effect of different exchangeable cation on the adsorption amount of MB, and showed that methylene blue cations (MB^+) replace Na^+ more easily than they do Fe^{3+} and Al^{3+}. Thus, it was necessary to determine the effect of the Na-solution on the MB SSA of soils. For this reason, one set of soils passing No. 40 were washed with NaCl. The results show that there is no significant difference between the measured MB SSA of the natural and Na-exchanged soils (Table 3). Based on the obtained results, it is concluded that there is no need for Na-treated samples for surface area measurements using MB methods.

6. Cation exchange capacity (CEC)

The CEC of the soils was determined by MB-spot test and NH_4-Na methods. The results show that the MB values are generally lower than the capacities obtained by the ammonium acetate method

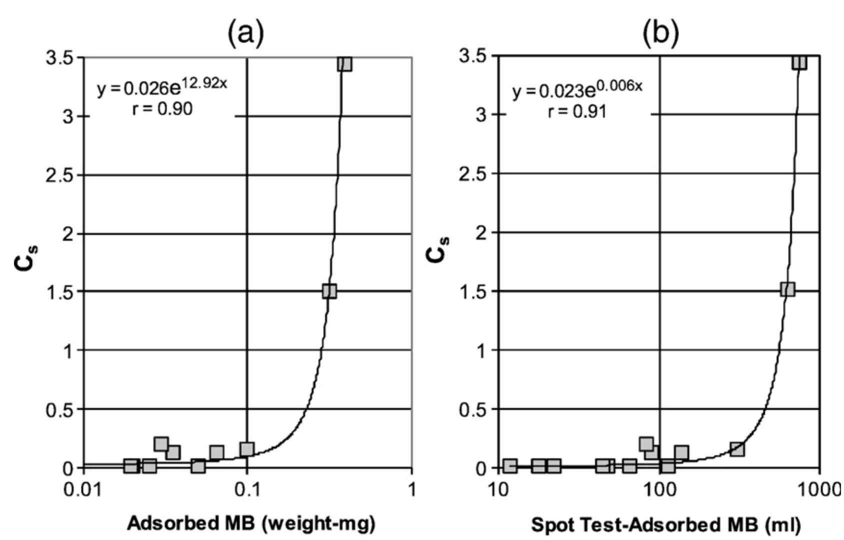

Fig. 5. Adsorbed MB at the completion point and swell index (C_s) relationships (a) MB-titration b) MB-spot test).

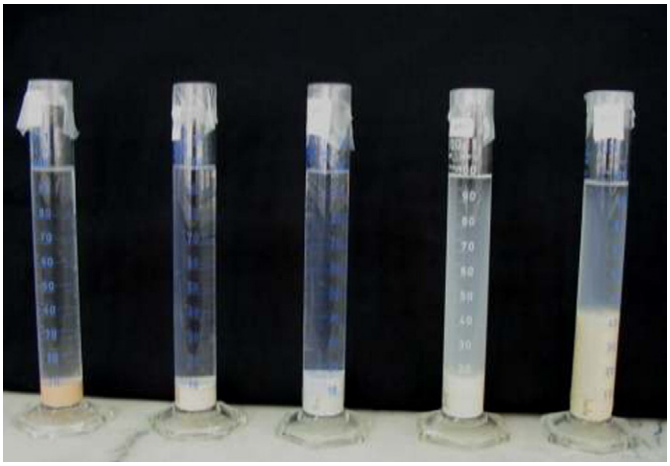

Fig. 6. Swell index determination of the samples.

(Table 4). Similarly, Taylor (1985), Soon (1988), and Wang et al. (1996) reported that most CEC values of clayey soils measured with NH_4-Na exchange were greater than those measured with MB method. Coleman and Harward (1953) reported that the difference between the two CEC determination methods is possibly caused by extensive aggregation, formation of H^+, or inhibition of MB sorption. However, our results reveal that the correlation coefficient between CEC-MB-spot test method and CEC-NH_4-Na method is 0.88 (Fig. 3). Similarly, Wang et al. (1996) reported correlation coefficient of 0.86 with MB-titration method. These results indicate that there are not much difference in the CEC values used two methods. However, note that the MB method yields very low CEC estimates especially for zeolitic soils (Soil 6–7) (Table 4). Therefore, it should be noted that the CEC estimates with MB methods is inconvenient for zeolitic soils.

In the literature, it is reported that the MB clearly shows high dependency of adsorption on the type of cations on the clay. Researchers reported adsorption is complete only when the sample is in the lithium (Li^+) and the sodium (Na^+) exchanged form. Kahr and Madsen (1995) observed that the CEC of clays can be determined by MB methods when soils are in the sodium exchange form and the pH is neutral. In order to determine the effect of Na^+ exchange on the CEC values of soils, the samples were saturated with 2 M NaCl and the CEC values of these samples was determined with spot test method. As

Table 6
Examples of expansive soil classification systems

Seed et al. (1962)		Holtz (1959)	
Swelling potential (%)	Degree of expansion	Plasticity index (PI)	Degree of Expansion
>25	Very high	>35	Very high
5.0–25.0	High	25–41	High
1.5–5.0	Medium	15–28	Medium
0–1.5	Low	<18	Low

seen from Table 4, there is no significant difference between the CEC values of the natural and Na-exchanged samples.

7. Swell index and swell potential

Swell index of the soils was determined by two different methods. Table 5 shows the swell index of the samples that was determined from the oedometer test. Swell index of the soil is calculated from the void ratio (e) and effective consolidation stress ($\bar{\sigma}_v$) (Fig. 4) as follows (Lambe and Whitman, 1979):

$$C_s = \frac{-\Delta e}{\Delta \log \overline{\sigma}_v} \quad (5)$$

where Δe= change in void ratio, $\Delta\log\bar{\sigma}_v$ = change in effective vertical stress. Fig. 4 shows the e-log $\bar{\sigma}_v$ diagrams of the some soils from the present study. Regression analyses were developed between the adsorbed MB at the completion point, and swell index (C_s) (Fig. 5). As seen from Fig. 5, there are significant relationships between the adsorbed MB and C_s using both titration (r=0.90) and spot test (r=0.91) methods. For the oedometer tests, the samples were reconstituted at their liquid limits. Thus, the obtained swell indexes (C_s) are dependent on intrinsic soil properties such as SSA and CEC. The exponential correlation between amount of adsorbed MB and SSA is reflected itself on the correlation between swell index (C_s) and adsorbed MB value.

According to other swell index method, swelling potential of the samples is determined in a 100 mL graduated cylinder as shown in Fig. 6. The calculated swell indexes of the samples are shown in Table 5. The swell volume of the samples is different from each other. The amount of the first and second samples (on the left) are 10±0.01 g

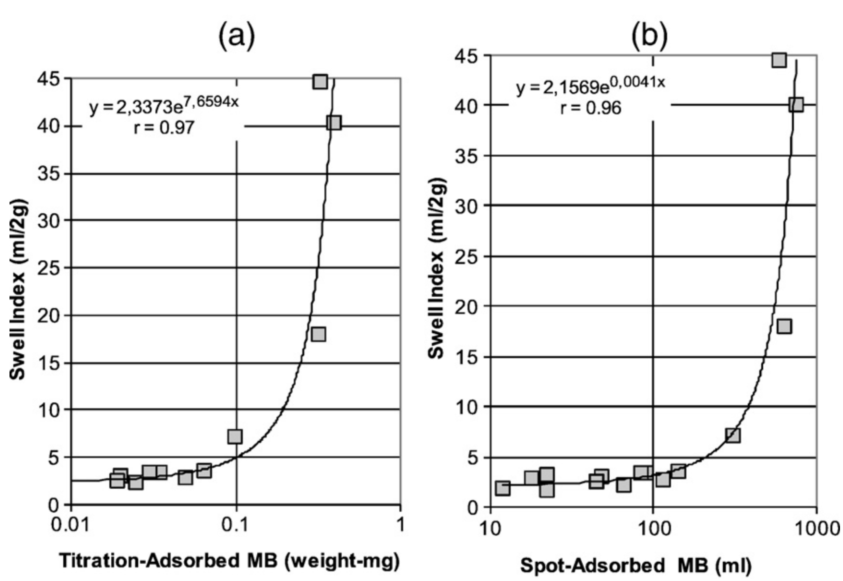

Fig. 7. Swell index and adsorbed MB relationship (a) titration b) spot test method).

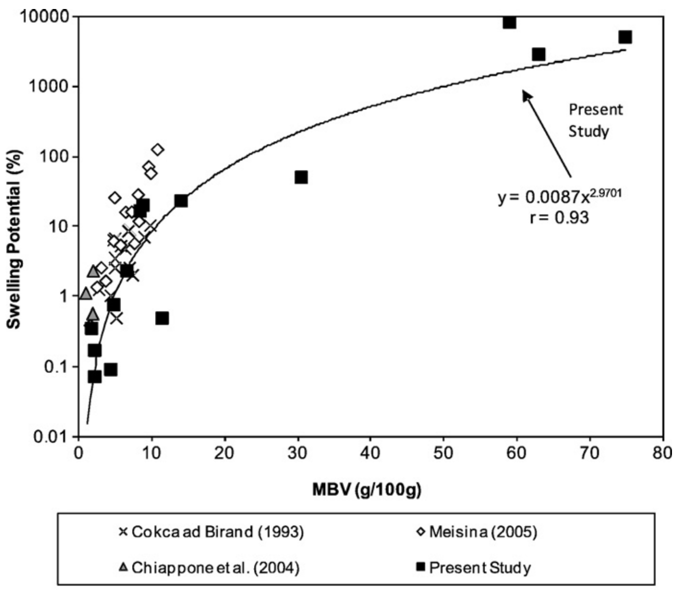

Fig. 8. Swelling potential and methylene blue value (MBV) relationship.

in the graduated cylinder, the others are 2±0.01 g. However, the swell volumes of the first and second samples are lower than those of the rest. This is because the first and second samples contain non-swelling clay minerals.

The results reveal that the correlation coefficient between the adsorbed MB and swell index is significantly high, r =0.97 and r =0.96 for titration and spot test, respectively (Fig. 7). Note that the sample #14 was omitted from correlations due to its unique characteristics such as having a SSA of 753 m^2/g MB-spot; yet, it has relatively low liquid limit (111.5%).

Researchers have attempted to predict the swell potential of soils using soil index properties such as plasticity index (PI), clay content, and activity (Holtz, 1959; Seed et al., 1962) (Table 6). For example, Seed et al. (1962) proposed that swelling potential of a soil can be determined for soils with clay content between 8% and 65% using the following empirical equation:

$$\text{Swelling potential}(\%) = S = \left(3.6*10^{-5}\right)*\left(\text{Ac}^{2.44}\right)*\left(\text{CC}^{3.44}\right) \qquad (6)$$

where Ac = Activity and CC = Clay Content. However, determining the activity and clay content is time consuming. Thus, researchers proposed alternative swelling prediction techniques for quick; yet,

Table 7
Swelling potential of soils as assessed by the different classifications

Swelling potential			
Sample #	Çokca and Birand (1993a)	Seed et al. (1962)	Holtz (1959)
S-1	Medium	Low	Low
S-2	Low	Low	Low
S-3	Low	Low	Low
S-4	Medium	Low	Low
S-5	Low	Medium	Medium
S-6	High	Low	Low
S-7	Low	Low	Low
S-8	Low	Low	Low
S-9	Very high	High	High
S-10	High	High	Very high
S-11	Very high	High	Very high
S-12	Very high	High	High
S-13	Very high	Very high	Very high
S-14	Very high	Very high	Very high
S-15	Very high	Very high	Very high
S-16	Very high	Very high	Very high

Table 8
Proposed swelling potential classification using methylene blue value (MBV)

Methylene blue value (g/100 g)	Degree of expansion
0–4	Low
4–8	Medium
8–15	High
>15	Very high

reliable swelling potential estimates. Methylene blue value is one of these promising techniques. According to Çokca and Birand (1993a), for 100 grams of fine soil "Methylene Blue Value (MBV)" is determined as follows:

$$\text{MBV} = V_{cc}/f' \qquad (7)$$

where $V_{cc}(cm^3)$ = Volume of methylene blue solution injected to the soil solution (the concentration of MB 10 g/L), f' (gr) = Dry weight of soil.

To evaluate the validity of this approach, we plotted the data of this study and those of previous researchers all together (Fig. 8). The swelling potential of the present study samples was determined by Eq. (6). As seen from Fig. 8, indeed there is a good correlation between MBV and swelling potential of soils. Further, note that there is a good agreement between the results of these study and those of previous researchers. Thus, the obtained results suggest that swelling potential of soils can be determined using the MB test method without needing to determine clay content and activity.

However, Çokca and Birand (1993a) proposed swelling potential classification based on clay content and MBV of soils. We used the proposed swelling classifications to determine swelling potential of the soils tested. Table 7 presents swelling potential estimations of the studied samples according to different classifications. As seen from Table 7, the swelling potential prediction methods are remarkably close. However, Table 7 reveals that clay content, in general, cannot yield accurate estimate of swelling behavior of soils. In other words, the type of clay minerals with respect to proportion of mineral to the total weight is an important variable in determining swelling potential. This is because, for example, one soil may contain 70% clay mineral that is non-swelling, a second soil may contain 30% clay mineral that is swelling. Under this circumstance, the latter soil may swell more than former. Thus, clay content alone cannot represent the swelling potential of soils. On the other hand, MBV represents the surface area of a soil. The higher the surface area is the larger is the attraction for water molecules. Thus, the results suggest that MBV is enough for accurate swelling potential estimates (Table 7). According to this classification, the boundary MBV values were determined for each swelling potential classification. Based on these boundary MBV values, it is proposed to use Table 8 to classify swelling potential of soils.

8. Conclusions

The suitability of the MB test for determining specific surface area, cation exchange capacity and swelling behavior of the soils having a wide range of mineralogy was investigated. The results show that the N_2 adsorption and MB methods yield widely different SSA values. The results further suggest that the MB test methods are applicable to a wide range of mineralogy for SSA determination, and give both external and internal surface area. The N_2 adsorption method yields accurate SSA values for non-welling clayey soils; however, it yields very poor estimates of SSA for swelling clayey soils. The MB-titration and MB-spot test methods yield similar results but MB-spot test method is simpler. The MB-spot test can be easily applied in the laboratory, but its accuracy is lower than the titration method.

Generally, the CEC values obtained using the MB test methods are lower than those obtained using the NH_4-Na method; but the two are linearly related. There is large difference for CEC values for zeolitic soils determined with these two methods. The MB-CEC values of the zeolitic soils are lower than those determined using NH_4-Na method. No significant difference was observed between MB determined CEC values of Na-exchanged soils and natural soils. It can be concluded that there is no need Na-saturated samples for these tests.

Correlation coefficients between the swell index and adsorbed MB values are 0.97 and 0.96 with titration and spot test methods, respectively. With respect these high correlation coefficients, it can be said that swelling potential can be estimated by MB test accurately and easily without time consuming clay content and activity determining tests.

A new swelling potential classification system is proposed based on MBV. This new classification system may be useful for mapping the swelling potential of large areas.

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