

## Characterization of Egyptian Smectitic Clay Deposits by Methylene Blue Adsorption

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**Abstract: Problem statement:** The characterization of smectitic clays has been traditionally made using physical and chemical methods which are time-consuming and require costly equipment. Adsorption of methylene blue by these clays has been introduced as a quick and cheap method for the estimation of cation exchange capacity and surface area. Therefore, the aim of the present study was to test the applicability of the methylene blue method for the determination of cation exchange capacity and specific surface area of Egyptian smectitic clay deposits and hence to estimate their content of expansive clays. **Approach:** The distribution of sand, silt and clay fractions was determined in the studied samples by grain size analysis. The methylene blue test was applied using the halo method for the determination of the optimum adsorption point. **Results:** A positive correlation was found between the cation exchange capacity of the claystone as determined by the methylene blue value and its clay fraction and between the specific surface area and the cation exchange capacity. **Conclusion/Recommendations:** It has been concluded that the methylene blue test can be used as a reliable and rapid method for the characterization of smectitic clay deposits and soils containing smectite. These properties are important for engineering and environmental geological assessments of sites for different construction purposes.

**Key words:** Cation exchange capacity, surface area, claystone, smectite, Methylene Blue Adsorption value (MBA)

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### INTRODUCTION

Smectitic clay deposits of Upper Eocene and later geological ages occur in several localities in Egypt. The most important of these are located in Fayoum Depression, in the North Western Coastal plain and along the Cairo-Alexandria, Cairo-Ismailia and Cairo-Ain Sukhna Desert Roads. The geology and mineralogy of these deposits have been described by several authors, for example by Attia (1996). These authors used X-ray diffraction and/or Fourier Transform Infrared for determining the composition of clay minerals present and chemical methods for the determination of cation exchange capacity of the clays. Such techniques are time-consuming and quite costly. No attempt has, hitherto, been made to use the much simpler methylene blue method to characterize these clay deposits.

Methylene blue is a large polar organic molecule which is adsorbed onto the negatively charged surfaces of clay minerals. It has high selectivity for adsorption by smectite and is also adsorbed by the smectite component of mixed-layer clays, but is largely

unaffected by other clay minerals. Adsorption of methylene blue is a common method used to estimate the cation exchange capacity, specific surface area, swell potential and smectite content of clays deposits and soils. A vast number of publications refer to the application of this method (Hang and Brindley, 1970; Lagaly, 1981; Kahr and Madsen, 1995; Chiappone *et al.*, 2004; and Yukselen and Kaya, 2008, among others). The methylene blue test has been used routinely by the drilling industry to estimate the percentage of bentonite mud in the circulation of fluids (API, 1982). It has been also become a standard method for the determination of cation exchange capacity and surface area of clays in a wide array of applications (ASTM, 2003). Yool *et al.* (1998) report on the inclusion of the methylene blue dye adsorption test in the European Standards for the determination of harmful fines in aggregates for concrete and mortar. Erguler and Ulusay (2003); Chiappone *et al.* (2004); Avsar *et al.* (2005) and Yukselen and Kaya (2008) used the methylene blue method to determine the swell potential of clays and soils. Used methylene blue to

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determine the clay content of Egyptian limestones in their evaluation of this rocks as construction materials for highway pavements.

The aim of the present work was to study the application of the methylene blue method as a tool for the characterization of Egyptian smectitic clay deposits. The clay deposits from Gebel Hamza-Gebel Um Qamar, along the Cairo-Ismailia road have been selected as an example to demonstrate the applicability of this technique.

## MATERIALS AND METHODS

Gebel Hamza-Gebel Um Qamar area lies north of the Cairo-Ismailia Desert Road, about 32 km from Cairo (Fig.1). The oldest exposed rocks in the area are of Oligocene age, represented by gravels, sands and sandstones with scattered silicified wood fragments and small outcrops of weathered basalt sheets. The Oligocene is followed unconformably by Miocene sediments which have been differentiated into two facies: a lower marine and an upper non-marine sequences. The marine facies is the main part of the Miocene section in the area and is divided into strata of Lower and Middle Miocene ages. The former attains a thickness of about 70 m at Gebel Hamza and is mainly composed of sand and sandstones interbedded by clay bands with varying thickness. The Middle Miocene strata unconformably overlie the Lower Miocene and are mainly composed of sandy limestone and dolostones interbedded with some clay layers. The non-marine Upper Miocene beds unconformably overlie the Middle Miocene and are composed of gravels and sands. The smectitic clay deposits in this area are mainly confined to the Lower Miocene and have been exploited from a number of small quarries in the area.

Sixteen samples of claystones were collected from Gebel Hamza and Gebel Um Qamar area the sand, silt and clay content of these samples was determined by wet sieving and sedimentation analysis (pipette method). The mineralogical composition of the clay fraction was determined by X-ray diffraction analysis according to the method described by Poppe *et al.* (2001).

The methylene blue test was carried out as follows: Two grams of the dried sample (at 100°C) were transferred into a conical flask and stirred in 100 mL distilled water for titration with standard methylene blue solution. The latter was prepared by dissolving one gram of dry methylene blue (Merck, with molecular weight of 319.9) in 250 mL of distilled water. The end point of titration of the methylene blue adsorption was determined with the halo method (Kahr and Madsen, 1995; Yukselen and Kaya, 2008).

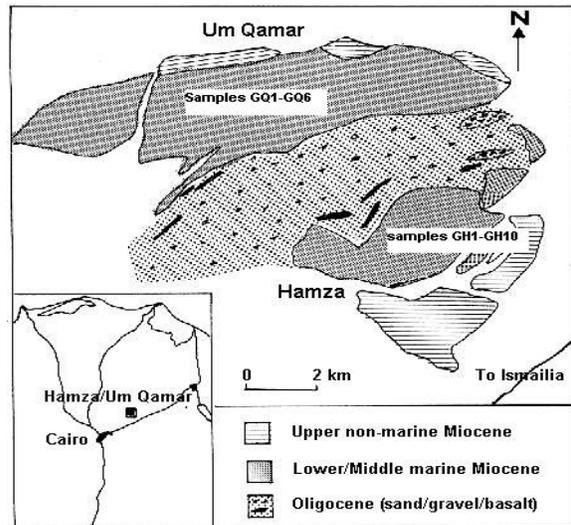


Fig. 1: Sketch Geological Map of G. Hamza and G. Um Qamar area

Small quantities of the methylene blue solution were gradually added from a burette to the stirred clay suspension in the conical flask and drops of this suspension were put with a glass rod on a filter paper. First a colourless waterfront spread in a circle on the filter paper, whereas the blue-coloured clay in the centre stuck to the paper. At the end point a light blue halo appeared. The clay suspension was then stirred two more minutes and the dotting test carried out to show whether a blue halo was shaped again. If so, this marked the end point of the test. Otherwise, further titration was carried out carefully until the halo did not disappear any longer after 2 min. It should be noted here that Kahr and Madsen (1995) used also an alternative method to determine the methylene blue adsorption. After addition of increasing quantities of methylene blue solution in a row of glass centrifuge tubes with the same clay content, the glass tubes were centrifuged and the remaining methylene blue concentration in the supernatant solution was measured photometrically at 620 nm. They concluded that the results are comparable to those obtained by the halo method, which is much simpler. Accordingly, the latter method has been used in the present study.

The Methylene Blue Adsorption value (MBA) has been calculated according to:

$$MBA = [(A/B) \times C] / (D/100)$$

Expressed in g/ 100 g of sample

Where:

A = The weight of dry methylene blue.

- B = The volume of methylene blue solution (1 litre)
- C = The volume of MB added to the sample until the end point is reached
- D = Is the weight of the dry powdered sample

The Cation Exchange Capacity (CEC) has been determined according to:

$$CEC = (100/D) \times C \times NMB$$

Expressed in meq/ 100 g

Where:

- D = The weight of the dry powdered sample.
- C = The volume of MB added to the sample until the end point is reached
- NMB = The normality of methylene blue and is =  $A/319.9$
- A = The weight of dry methylene blue to be dissolved in one litre of distilled water
- 319.9 = Molecular weight of methylene blue

The Specific Surface Area (SSA) is calculated according to:

$$SSA = (m(MB)/319.9) \times \text{Avogadro's Number} \times A_{MB} \times (1/A) \text{ expressed in m}^2/\text{g}$$

Where:

- m(MB) = The mass of adsorbed methylene blue at the point of complete cation replacement (end point)
- Avogadro's Number =  $6.02 \times 10^{23}/\text{mol}$
- $A_{MB}$  = The area covered by one methylene blue molecule, typically assumed to be  $130 \text{ \AA}^2$ , according to Hang and Brindley (1970)

### RESULTS

Table 1 gives the results of textural analysis of the clay samples, from which it appears that the clay deposits are mainly classified as claystone, with some as silty claystone and one sample as clayey siltstone, according to Picard's nomenclature (Picard, 1971). The X-ray powder diffraction analysis of the separated clay fractions revealed that the main clay mineral present is smectite (estimated to be between 30 and 70%), followed by kaolinite (15-0%) and illite (0-7%). This wide variation in texture and composition of the clay minerals present enabled the thorough testing of the methylene blue method.

Table 2 gives the results of determination of the Methylene Blue value (MBA), Cation Exchange Capacity (CEC) and the Specific Surface Area (SSA) of the bulk claystone samples and of the clay fractions in these samples.

### DISCUSSION

The clay fractions in the studied samples have higher MBA, CEC and SSA than the parent claystone samples because methylene blue is adsorbed mainly on the clay fraction, but not on the sand and silt fractions which are composed mainly of quartz and other detrital minerals. Figure 2 shows the positive correlation ( $r = 0.73$ ) between the CEC of the claystones and their respective clay fractions. The deviation from a perfect correlation and the scatter of some points are due to the variation of the clay content in the claystone samples and also due to the variation of the smectite content in the clay fractions.

Table 1: Textural Analysis of clay deposits

Sample No.	Clay (%)	Silt (%)	Sand (%)	Nomenclature
GH1	62	32	6	Silty claystone
GH2	79	20	1	Claystone
GH3	71	27	2	Silty claystone
GH4	80	16	4	Claystone
GH5	85	13	2	Claystone
GH6	75	23	2	Claystone
GH7	75	21	4	Claystone
GH8	76	16	8	Claystone
GH9	80	13	7	Claystone
GH10	65	31	4	Silty Claystone
GQ 1	55	41	4	Silty claystone
GQ 2	75	21	4	Claystone
GQ 3	76	21	3	Claystone
GQ 4	76	20	4	Claystone
GQ 5	70	25	5	Silty Claystone
GQ 6	45	35	20	Clayey siltstone

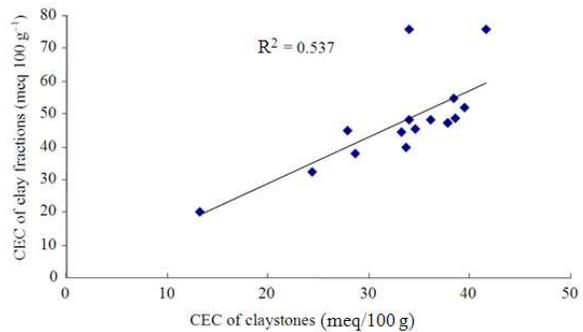


Fig. 2: Relationship between CEC of claystones and of their clay fractions

Table 2: CEC and Specific Surface area of smectitic clays

Sample No.	Clay % in sample	MBA (g/100 g)		CEC (meq/100 g)		SSA (m <sup>2</sup> /g)	
		Claystone	Clay frac.	Claystone	Clay frac	Claystone	Clay frac
GH1	62	8.92	14.39	27.89	44.99	218.3	352.1
GH2	79	12.31	15.58	38.52	48.72	301.1	381.1
GH3	71	10.89	15.35	34.06	47.99	266.6	375.6
GH4	80	12.08	15.10	37.76	47.20	295.4	369.2
GH5	85	10.78	12.68	33.70	39.66	263.6	310.2
GH6	75	7.98	10.40	24.38	32.51	190.7	254.3
GH7	75	10.64	14.18	33.26	44.35	260.1	346.9
GH8	76	17.99	23.68	28.67	37.72	224.3	295.2
GH9	80	12.08	15.10	37.76	47.21	295.5	369.5
GH10	65	4.22	6.49	13.20	20.31	103.1	158.8
GQ 1	55	9.52	17.31	41.60	75.66	232.8	423.5
GQ 2	75	14.06	18.75	36.20	48.28	346.5	462.0
GQ 3	76	11.09	14.59	34.66	45.61	271.2	356.8
GQ 4	76	12.62	16.62	39.46	51.95	308.7	406.4
GQ 5	70	12.30	17.57	38.44	54.92	300.8	429.8
GQ 6	45	10.89	24.21	34.04	75.67	266.4	592.2

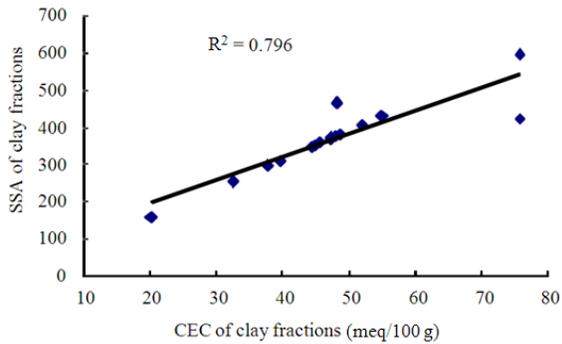


Fig. 3: Relationship between SSA and CEC of Clay fractions

Because of the high selectivity of methylene blue to be adsorbed on smectite rather than on other clay minerals, the CEC value of a claystone is considered a proxy for its smectite content. Therefore, the methylene blue method can be used as a reliable and rapid method for estimating the content of expansive clay minerals (smectite and smectite inter-layer minerals) in a clay deposit or soil.

Figure 3 shows the relationship between the CEC of the clay fractions and their SSA. The almost perfect correlation between both ( $r = 0.89$ ) is due to the dependence of the SSA on the smectite content in the clay fraction.

### CONCLUSION

From the present study, it can be concluded that the methylene blue method can be used to determine the CEC (and consequently the smectite content) and the SSA of claystones, soils and other finely-ground rocks containing expansive clay minerals. This can provide a

useful and quick tool in a wide range of applications in engineering geology and in environmental geology. For example, the testing of foundations for the presence of expansive clays is important for the sound construction of different infrastructures. The determination of CEC and SSA are also important for the selection of sites to be used as landfills and for lining purposes.

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