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Methylene Blue Adsorption by Clays Saturated with Different Inorganic Cations

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Clay fractions of five contrasting Malaysian soils obtained by the sedimentation method were saturated with various inorganic ions (H^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Al^{3+}, PO_4^{3-}). Adsorption isotherms were determined for methylene blue adsorbed from aqueous solutions on the clays. It is shown that compared with monovalent cations, divalent cations are more difficult to be displaced by methylene blue cation. The cation-exchange capacities determined by this method decreased in the order: $H^+ \sim Na^+ > PO_4^{3-} > K^+ > Mg^{2+} > Ca^{2+}$. In addition specific surface areas were calculated and compared for the various clays.

The relative ability of soils to retain cations, anions and molecules is determined to a large extent by their surface areas, types of clay minerals and the amount of organic matter. Several workers[1–6] have attempted to use the methylene blue dye adsorption from aqueous solution as a method to measure cation-exchange capacity (CEC) as well as specific surface areas of the adsorbing materials. In isotropic studies using ^{22}Na as a tracer, Brooks[1] established that methylene blue dye adsorption can nonetheless be used as a rapid, approximate method for estimation of CEC of siliceous minerals like montmorillonite and kaolinite. Brindley and Thompson[3] showed that CEC of Li- and Na-saturated clays determined by methylene blue adsorption agreed with values obtained by conventional titration techniques. Specific surface areas of the clays can also be determined from the amount of methylene blue adsorbed on the clay to produce optimum flocculation. Cation-exchange capacities of kaolinitic clays in the H^+- forms as determined by methylene blue adsorption were found to be equal to CEC measured from Ba^{2+} exchange[7].

For Malaysian soils under *Hevea*, exchange studies were mainly confined to the equilibrium reactions of the ion pairs K:Al, Mg:Al and K:Mg[8]. Preferential adsorption of one cation to another was found to depend on the types of soils and the total electrolyte concentrations. Recently, Lau[9] reported the use of a cation-exchange resin for assessing the relative amounts of K and Al which are either in the exchangeable or non-exchangeable forms.

In view of the annual application of N, P, K, Ca and Mg fertilisers to *Hevea* and the effects the respective cations or anions have on the exchange properties of the soils, this paper reports the use of a large organic ion such as methylene blue, to assess the replaceability of the various inorganic cations in the clay complexes, the CEC and the specific surface areas of the clays.

EXPERIMENTAL

Subsoil (15–45 cm) of five contrasting soil series were sampled, air-dried (28°C) and ground to pass through a 2 mm sieve. Mechanical composition and some chemical properties of the soils are given in *Table 1*.

COMMUNICATION 632

TABLE 1. PHYSICAL AND CHEMICAL ANALYSES OF SUBSOILS (<2 mm)

Soil series	Great Soil Group (Soil Taxonomy)	pH	Sand (%)	Silt (%)	Clay (%)	Exchangeable cations ($1N$ NH_4OAc) m-equiv./100 g soil				Cation-exchange capacity m-equiv./100 g soil
						K^+	Ca^{2+}	Mg^{2+}	Al^{3+} [a]	
Rengam	Red and Yellow Podzolic (Paleudults)	4.3	41.3	8.0	50.7	0.04	0.22	0.06	2.48	3.04
Batu Anam	Red and Yellow Latosol (Dystropepts)	4.4	19.3	22.5	58.2	0.07	0.25	0.07	4.33	4.60
Kuantan	Latosol (Haplorthox)	4.4	10.5	24.4	65.1	0.02	0.19	0.04	2.08	2.83
Serdang	Red and Yellow Podzolic (Tropudult)	4.2	60.1	13.2	26.7	0.02	0.08	0.02	2.93	3.40
Selangor	Humic Gley (Sulfaquepts)	4.2	8.1	32.8	59.1	0.09	0.24	0.13	12.50	18.60

[a] By $1N$ KCl extraction

Adsorption Isotherms

Clay fractions ($<2\mu m$) of the five soils studied were separated by the pipette method of Piper[10]. Saturation of the clays with different cations (Na^+, H^+, K^+, Mg^{2+}, Ca^{2+} and Al^{3+}) were carried out by treating the clays with successive portions of $0.5N$ solutions of the respective chlorides until the concentration of chloride solution that came through remained unchanged. The clays were then washed by centrifugation with distilled water until the washings were chloride-free (Ag NO_3 test).

Adsorption isotherms for methylene blue adsorbed from aqueous solutions on the various clays were determined by a procedure similar to that of Brindley and Thompson[3]. Ten millilitre aliquots of clay suspension which were previously diluted to about 2 mg per litre were added to 40 ml of methylene blue solution at pH 4.5 (NaOAc/HOAc buffer) and concentrations ranging from 1×10^{-3} to 26×10^{-3} mmoles per litre. The combined clay suspension and dye solution were shaken and left to equilibrate (23°C) overnight before separation of the adsorbents by centrifugation. The concentration of the dye in the supernatant solution was determined by a Spekker (Hilger) colorimeter using Filter No. 8 and a 2 cm cell. The amount of dye adsorbed corresponds to the difference between the initial and final concentrations of the dye solution. The condition for optimum flocculation by methylene blue for each clay suspension was determined by the procedure of Hang and Brindley[2].

RESULTS AND DISCUSSION

Data showing the physical and chemical properties of the five sub-soils (<2 mm size) are given in *Table 1.* The texture of the soils varied from sandy loam (Serdang series) to silty clay (Selangor series). Generally, the soils were highly acidic (pH 4.2 to 4.4), low in exchangeable cations (K^+, Ca^{2+} and Mg^{2+}) and dominated by aluminium ions. Cation-exchange capacities for the Selangor and Batu Anam series soils were relatively high. Recent work had shown the presence of montmorillonite in the Selangor series soils; and both Serdang and Batu Anam series soils contained trace quantities of illite[8,11].

Adsorption Isotherms

Adsorption isotherms for the Selangor, Serdang and Rengam clays saturated with various cations are shown in *Figures 1, 2* and *3* where the adsorbed methylene blue in milliequivalent per 100 g clay is plotted against the corresponding initial dye concentration expressed in millimole per litre. The adsorption isotherms rise linearly from the origin and start to flatten when the initial dye concentration exceeds 0.016 millimole per litre. Beyond this value, little further adsorption of the dye by the clays is obtained indicating that a saturation state is reached or approached. Differences in the adsorption isotherms were found when different exchangeable inorganic cations were present in the clays.

Cation-exchange Capacities

Cation-exchange capacities of the various clays based on maximum adsorption of methylene blue by the clays were obtained from the adsorption isotherms *(Table 2).* Compared with CEC determined by $1N$ NH_4OAc, CEC values obtained by methylene adsorption are low. The differences vary from 8% to 20% for clays from four soils, Serdang, Rengam, Batu Anam and Kuantan; and 30% for Selangor clays from Selangor series. It is seen that divalent cations are more difficult to be displaced by methylene

TABLE 2. CATION-EXCHANGE CAPACITIES OF CLAYS BY METHYLENE BLUE ADSORPTION

Soil series	Cation-exchange capacities (m-equiv./100 g clay)							Cation-exchange capacities (1N NH_4OAc) m-equiv./100 g clay
	Na^+	H^+	K^+	Mg^{2+}	Ca^{2+}	Al^{3+}	PO_4^{3-}	
Rengam	5.9	6.0	5.0	4.4	4.1	4.9	5.6	7.60
Batu Anam	11.0	10.4	4.3	4.1	3.8	4.2	5.5	12.50
Kuantan	7.2	7.2	5.8	5.1	4.5	4.2	6.3	8.43
Serdang	10.3	10.4	9.4	9.1	8.8	8.2	10.2	11.30
Selangor	28.2	29.4	27.5	22.7	22.0	25.0	27.8	40.23

blue cation than the monovalent cations, thus giving rise to lower CEC values for clays saturated with divalent cations. For cations with similar charges, the replacing power of methylene blue tends to decrease with increasing size of the cation. The CEC values were shown to decrease in the order: $H^+ \sim Na^+ > K^+ > Mg^{2+} > Ca^{2+}$. Greater affinity of the clays for Ca^{2+} and Mg^{2+} has been shown to be due to hydration of the cations[12].

Cation-exchange capacities of Al^{3+} clays as determined by methylene blue appeared to be higher than those of Ca^{2+} or Mg^{2+} clays of Rengam, Batu Anam and Selangor series soils. The reverse was obtained for the Kuantan and Serdang clays. Coulter[13] showed that CEC of K^+- or Ca^{2+}-saturated clays remained constant when the equilibrating solutions of $AlCl_3$ had a pH of 3. At pH 4, changes in CEC were observed and these were explained by the adsorption of aluminium from solutions as Al^{3+} and $Al(OH)_2^+$. In view of the fact that the aqueous methylene blue solutions for the equilibration studies were buffered to pH 4.5, cation exchange between the methylene blue ion and aluminium would involve not only Al_3^+ and $A(OH)_2^+$ but also other polymeric forms of aluminium[14]. The extent to which such exchange reactions take place cannot be adequately explained under the present study.

Treatment of the various clays with 0.5N tripotassium phosphate solution seemed to give higher CEC values than those of K^+-, Ca^{2+}-, Mg^{2+}- and Al^{3+}-saturated clays. The highly weathered acidic soils of Malaysia had been noted for its high phosphate fixing capacities. Reduction of free sesquioxides through reaction of PO_4^{3-} with Fe and Al oxides followed by subsequent alteration of the exchange complex through phosphation had possibly increased the CEC of the clays. Similar observations were reported by Perkins[15] who carried out laboratory investigations on soils and clays treated with phosphoric acids.

Specific Surface Area

The specific surface areas of the various clays were calculated from the amounts of methylene blue adsorbed on the clays to produce optimum flocculation by taking the

TABLE 3. SPECIFIC SURFACE AREAS OF NA + -SATURATED CLAYS BY METHYLENE BLUE ADSORPTION

Soil series	Specific surface area (m^2/g clay)
Rengam	34.0
Batu Anam	52.3
Kuantan	26.2
Serdang	46.5
Selangor	136.4

area per adsorbed molecule as 130 Å^2, which corresponds to the molecules lying flat on the clay mineral surfaces[2,3]. The condition for optimum flocculation for the Selangor, Serdang and Rengam series soils is shown in *Figures 1–3*. For specific surface area determination by adsorption of ions in solutions, other workers[2,16,17] converted the clay to the H^+ or Na^+ form. The specific surface areas of the various clays in the Na^+

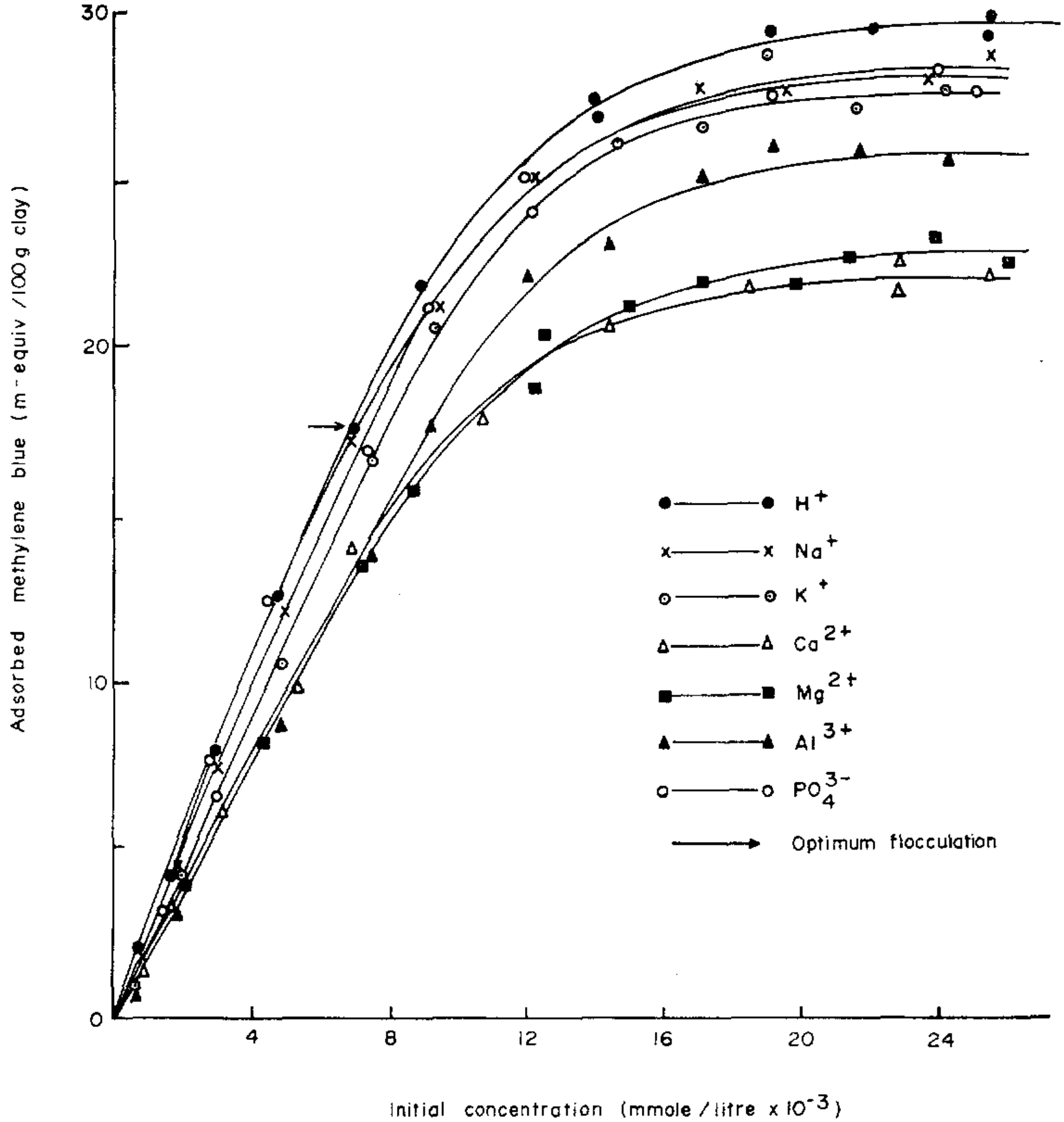

Figure 1. Methylene blue adsorption by clays saturated with different inorganic cations – Selangor series soil.

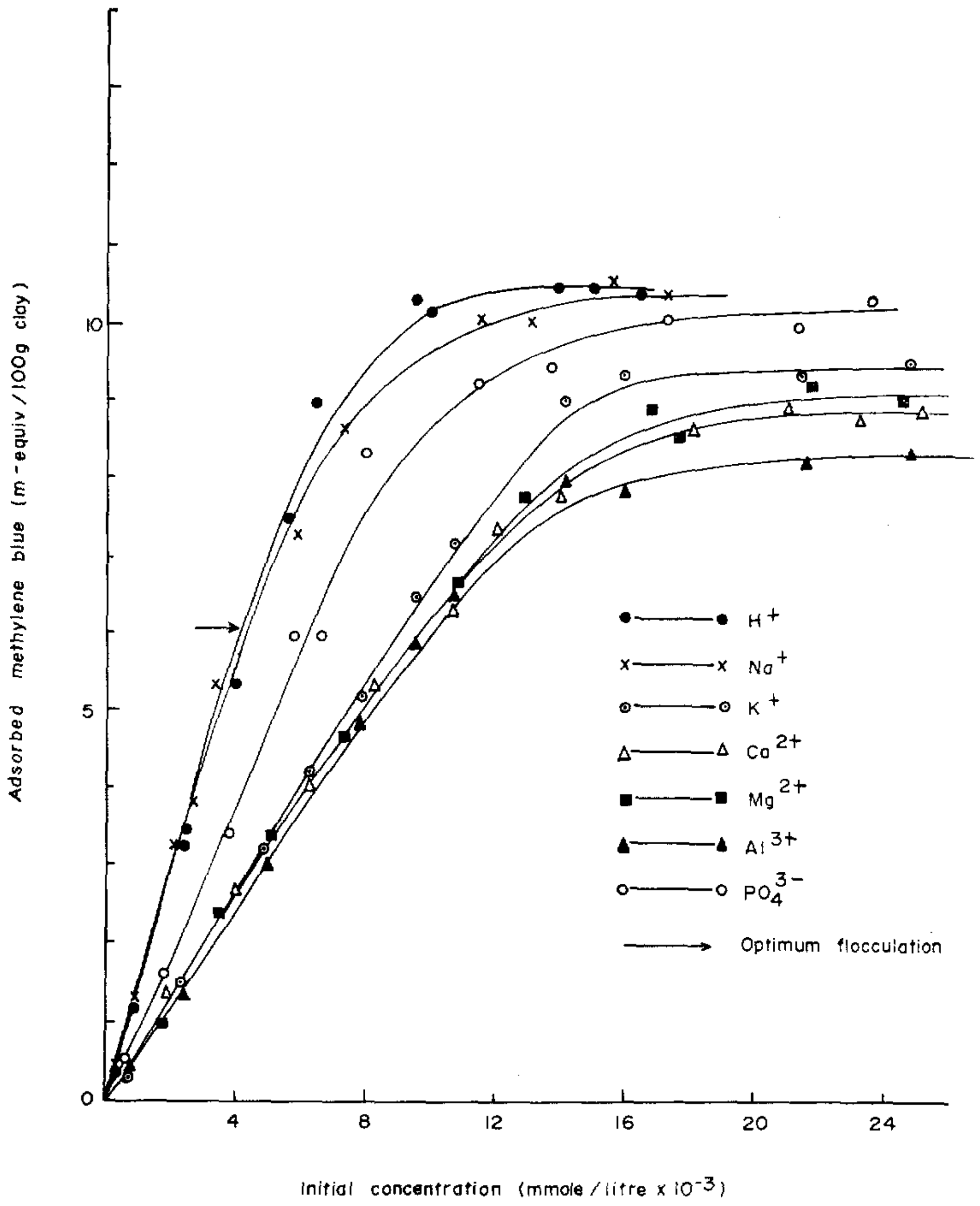

Figure 2. Methylene blue adsorption by clays saturated with different inorganic cations – Serdang series soil.

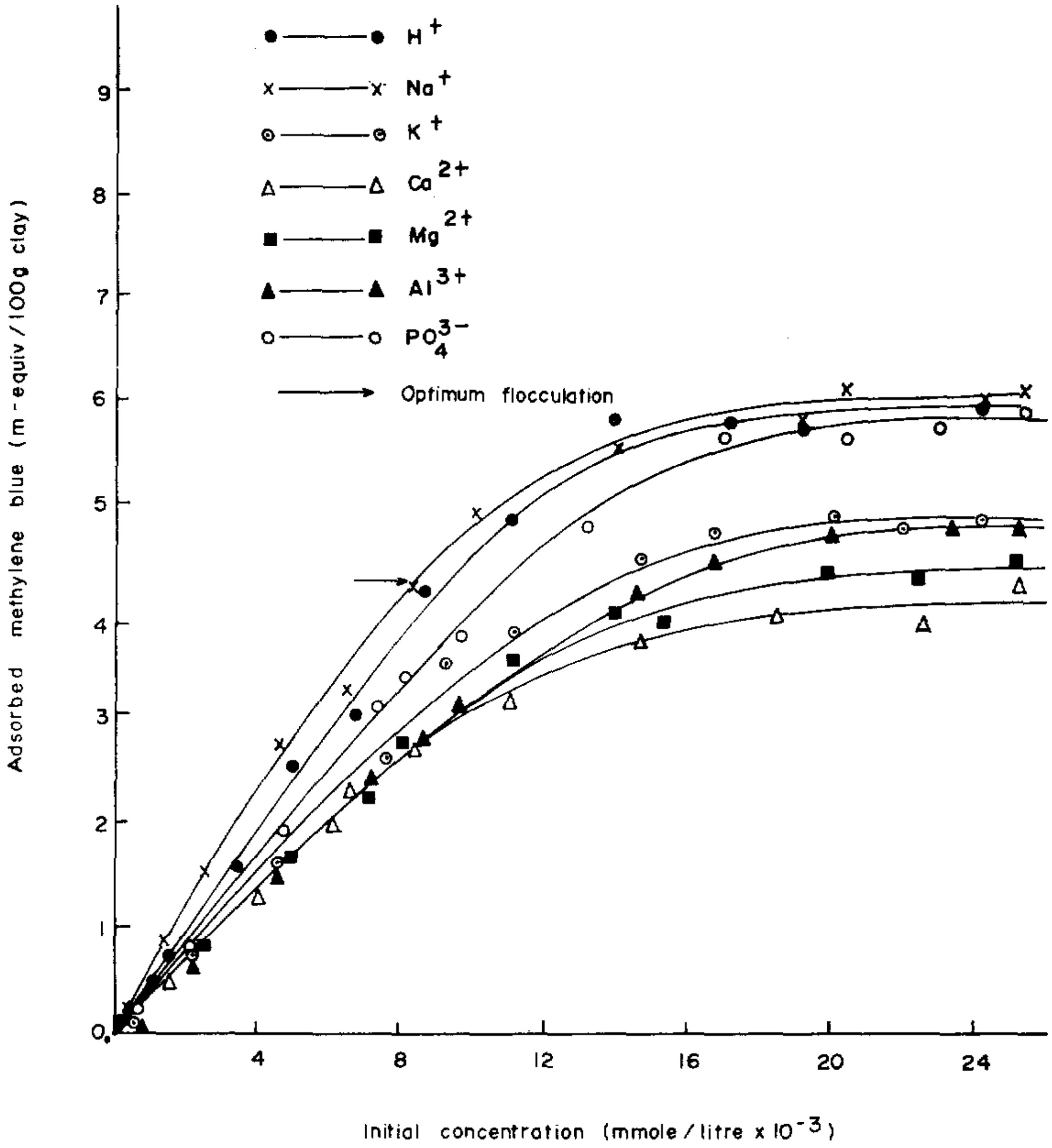

Figure 3. Methylene blue adsorption by clays saturated with different inorganic cations – Rengam series soil.

form were determined *(Table 3)*. Specific surface area is relatively high for clays of the Selangor, Serdang and Batu Anam series soils which have been shown to contain 2:1 type of minerals. Particularly, in the Selangor series soil which contains a significant amount of expanding montmorillonitic clay (>5%), the specific surface area as determined by this method includes both the internal and external areas.

CONCLUSION

An alternative method using methylene blue dye adsorption has been shown to be useful for assessing the relative retention powers of the various clays towards the cations; H^+, Na^+, K^+, Ca^{2+}, Mg^{2+} and Al^{3+}. With the exception of the Selangor series soil which contains some montmorillonite, agreement in CEC values determined by the methylene blue adsorption method and the conventional method of using 1*N* NH_4OAc was fairly good. Under suitable conditions, specific surface areas can be derived and compared for the different soils.

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