

Determination of Specific Surface Areas of Clay Fractions of Soils under Rubber by Adsorption of Cetyl Pyridinium Bromide

LAU CHEE HENG* AND CHEN SEONG FONG**

Clay fractions from five contrasting soils under rubber cultivation were separated and their specific surface areas determined by adsorption of cetyl pyridinium bromide from solution. Results obtained showed that the specific surface areas of inland soils determined by the cetyl pyridinium bromide technique were comparable with those determined by adsorption of methylene blue at optimum flocculation. The specific surface areas of the clay were related to the release and adsorption of magnesium and aluminium by the soils. The cetyl pyridinium bromide technique can be used as an alternative method for the rapid determination of the specific surface areas of inland soils which contain predominantly non-expanding clay minerals.

Of the three major fractions in the soil, viz. clay, silt and sand, the clay fraction is the most reactive. The relative reactivity of the clay is determined not only by their mineralogy but also by their specific surface areas. Specific surface areas of the clay fractions of some Malaysian soils determined from the amount of methylene blue adsorbed on the clay to produce optimum flocculation were found to relate to the cation-exchange capacities of the clay¹. These clay fractions which had different specific surface areas had different preferences for H^+ , Na^+ , K^+ , Ca^{2+} , Al^{3+} and PO_4^{3-} ions. Lau² also showed that total specific surface areas of soils played an important role in the exchange behaviour of K^+ and Mg^{2+} ions and their release characteristics.

Besides methylene blue, other polar molecules like ethylene glycol, O-phenanthroline and cetyl pyridinium bromide (CPB) have been used to determine the specific surface areas of soils and clay^{3,4}. Comparing the surface areas of a range of soils and clay determined by the adsorption of CPB from solution and nitrogen, Greenland and Quirk^{5,6} found that there was very good agreement in the results when no expanding lattice material was present. In this

paper, the CPB technique is used to determine the specific surface areas of clay obtained from five contrasting soils under rubber. The results obtained are compared with the values measured by the methylene blue method reported earlier¹. In connection with this study, the relationships between the specific surface areas of clay and the rates of release of potassium, magnesium and aluminium from the clay are also discussed.

EXPERIMENTAL

Surface-soils (0-15cm depth) of contrasting physical and chemical properties were collected from five major areas under *Hevea* cultivation in Peninsular Malaysia. Details of the soils are given in Table 1. The soils sampled in bulk from either the unmanured plots or in between tree-rows where no fertilisers were applied, were dried in an air-oven at 45°C and passed through a 2 mm roller-sieve.

Separation and Treatment of Clay Fractions

To remove organic matter 20 g soil (<2 mm) were repeatedly treated with 15 ml 10% H_2O_2 . When the oxidation process was completed, the

*Rubber Research Institute of Malaysia (RRIM), P.O. Box 10150, Kuala Lumpur, Malaysia

**Present address: LRC (M) Sdn. Bhd., Kulim Industrial Estate, 09000 Kulim, Kedah, Malaysia

TABLE 1. DESCRIPTION OF THE SOILS

No.	Soil series	Soil order	Parent material	Mechanical composition (% on oven-dried soil, 105°C)				Clay minerals ^a						
				Coarse sand	Fine sand	Silt	Clay	Kaol.	Mont.	Ill.	Mica	Gibb.	Goeth.	Quartz
1	Durian	Ultisol	Siliceous shale	9.9	13.7	31.6	44.8	D	nd	X	X	nd	nd	X
2	Kuantan	Oxisol	Basalt	5.6	7.3	27.1	60.0	D	nd	nd	nd	X	X	t
3	Munchong	Oxisol	Shale	6.4	14.7	29.0	49.9	D	nd	nd	nd	X	X	t
4	Rengam	Ultisol	Granite	38.2	9.5	9.8	42.5	D	nd	nd	t	t	t	nd
5	Selangor	Inceptisol	Mixed marine deposits/ alluvium	0.8	9.6	41.1	48.5	D	X	X	t	nd	nd	t

^aAfter Singh⁸ and Noordin⁹: Kaol. = kaolinite; Mont. = montmorillonite;

Ill. = illite; Gibb. = gibbsite; Goeth. = goethite

D = dominant (>50%); X = significant (>5%); t = trace (<5%); nd = not determined

clay fraction was separated by the sedimentation and pipette method of Piper⁷. After obtaining sufficient material, the combined clay samples of each soil were made homo-ionic with respect to sodium by washing with successive 50 ml portions of 0.5 M sodium chloride solution until the chloride in the wash solution was unchanged. The homo-ionic clay washed till chloride-free with distilled water (silver nitrate test) was dried at 45°C and kept for determination of specific surface areas.

Determination of Specific Surface Areas

Samples of clay weighing between 0.5 g and 1.0 g were shaken with 50 ml portions of CPB solutions of concentrations ranging from 0.01 g to 0.20 g CPB per 100 ml solution at room temperature for 16 h. The clay suspension was centrifuged and the concentration of CPB in the supernatant liquid determined by comparing the ultra-violet adsorption of the solution with those of CPB standard solutions at 259 m μ using a Hilger-Watts 'Uvispek'. From the initial and final CPB concentrations, the adsorption of CPB by the clay fraction was calculated⁶.

Adsorption isotherms for CPB adsorbed from aqueous solutions on the various clay fractions were plotted (*Figure 1*). Following this, the specific surface area of each clay sample was determined from the maximum CPB adsorption which corresponds to the 'plateau' of the isotherm and the mean area covered by each adsorbed cetyl pyridinium ion. Assuming that no inter-lamellar adsorption occurs and the external surface coverage is 0.27 nm² per cetyl pyridinium ion, the apparent surface area is related to the amount of CPB adsorbed by the equation,

$$S = 162a \quad \dots 1$$

where S is the apparent specific surface area in square metres per gramme clay and a , the maximum amount of CPB adsorbed in milliequivalent per gramme clay.

The CPB in this study was re-crystallised five times with dried re-distilled acetone before it was left in a vacuum desiccator to dry over sulphuric acid. A plot of surface tension against

concentration of CPB showed that the sample was of about 98% purity.

RESULTS AND DISCUSSION

The soils selected for this study were derived from different parent materials (*Table 1*). The combined clay and silt contents of the soils varied from 89.6% in the Selangor series to 52.3% in the Rengam series. The total amount of coarse and fine sand in the soils ranged from 47.7% in the Rengam series to 12.9% and 10.4% in the Kuantan and Selangor series, respectively. Based on the clay mineralogical data obtained by Singh⁸ and Noordin⁹, the common clay minerals in the soils were kaolinite, goethite, gibbsite, illite and quartz; the lesser ones were mica, chlorite, vermiculite and montmorillonite. The clay fraction of the Durian series soil contained a significant amount of illite and mica while that of the Selangor series contained montmorillonite, illite and a trace amount of mica. In contrast to these two soils, the clay fractions of Kuantan and Munchong series contained appreciable amounts of goethite and gibbsite and that of Rengam series was dominated by kaolinite.

Adsorption of Cetyl Pyridinium Bromide

CPB adsorption isotherms for the clay fractions are shown in *Figure 1*. It is apparent that the adsorption isotherms for different clay fractions were different and in all cases, the maximum adsorption was reached after the concentration of the equilibrium CPB solutions was in the range 0.02–0.05 g/100 ml. The maximum CPB adsorption which corresponds to the 'plateau' of the isotherm varies with the clay fractions and increases in the order: Kuantan < Rengam < Munchong < Durian < Selangor.

Specific Surface Areas of Soil Clays

Based on the assumption that no inter-lamellar adsorption occurs and the external surface coverage is 0.27 nm² per cetyl pyridinium ion, the apparent specific surface area of each soil clay was determined from *Equation 1*. The specific surface areas of the

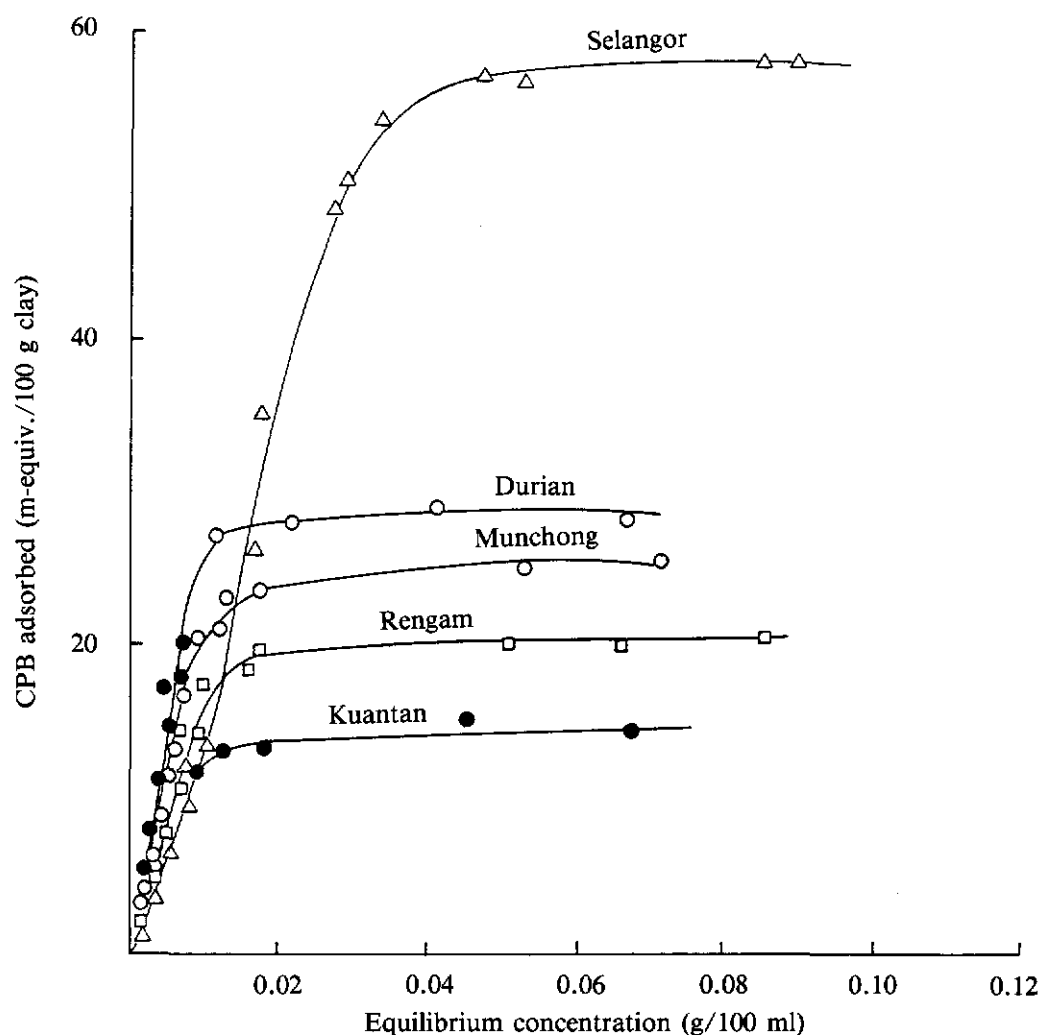


Figure 1. Cetyl pyridinium bromide adsorption isotherms for clay fractions.

soil clays are given in Table 2. Clay from Selangor series soil has the highest value while that from Kuantan series soil has the least value. The variations observed in the specific surface areas indicate that the materials obtained from different soils have contrasting surface properties. Indeed, Selangor series soil which contains a significant amount of 2:1 minerals, especially montmorillonite, and a high cation-exchange capacity shows complete dissimilarity in surface areas when compared with the other soils which are dominated by 1:1 minerals.

In addition, scanning electron micrographs of the Na-saturated clay taken at a magnification of 4000 times showed that the various soil clay had different textural properties and shapes². Clay from Durian series soil is made up of flake-like and crystal-shape materials which are identified as mica and kaolinite by transmission electron microscopy and X-ray diffractograms. On the other hand, clay from Selangor series soil consists of particles and fragmented microstructures of various sizes and shapes. The fragmented microstructures are associated

TABLE 2. SURFACE AREAS OF CLAY FRACTIONS DETERMINED BY CPB ADSORPTION

No.	Soil series	Maximum CPB adsorption (m-equiv./100 g clay)	CEC ^a (m-equiv./100 g clay)	Apparent surface area (m ² /g)	Surface area by methylene blue adsorption ^b (m ² /g)	Area (nm ²) per charge based on CPB area
1	Durian	28.76	19.2	46.6	48.4	0.40
2	Kuantan	14.76	13.5	23.9	26.2	0.29
3	Munchong	25.26	14.6	40.9	46.7	0.47
4	Rengam	20.02	11.3	32.4	34.0	0.48
5	Selangor	58.26	34.4	94.4	136.4	0.46

^aCation-exchange capacity of clay fraction by 1N NH₄OAc at pH 7.0^bLau and Chen¹

with biorelicts from shells of molluscs and chinoderms and plant remains, while the particles are kaolinite and 2:1 minerals. The clay of Munchong and Kuantan series soil are composed of very fine particles which are mainly kaolinite, gibbsite, goethite and some quartz.

Although there appeared to be differences in specific surface areas, particularly in the clay of Durian, Munchong, Rengam and Selangor series soils, the area per unit charge in each clay is fairly constant and falls within a narrow range of 0.40 – 0.48 nm² per unit charge. It is of interest to note that clay from Selangor series soil which has the largest specific surface area has area per unit charge similar to those of Durian, Munchong and Rengam series soils. On the other extreme, clay from Kuantan series soil has low surface area per unit charge. Under humid tropical conditions, clay which are dominated by kaolinite, hydrous aluminium and iron oxides have 'variable charges' which depend on the properties of the surrounding soil solution^{10,11}. It is therefore difficult to determine the relationship between surface charges and specific surface areas of clay fractions in this study. Finally, there is ample evidence that the conventional method of using neutral 1M ammonium acetate to determine the cation-exchange capacity and hence surface charges is not suitable¹².

Comparison of Specific Surface Areas Determined by the Methylene Blue Absorption Technique

The specific surface areas determined by the CPB method were generally lower than those obtained by the methylene blue absorption technique (*Table 2*). With the exception of clay from Selangor series soil, agreement between the two sets of values was found to be satisfactory and the maximum variation of about 12% was observed in clay from Munchong series soil. Under aqueous condition, the adsorption of CPB and methylene blue molecules is subjected to the interaction of the polar molecules with the soil surface and between themselves. Consequently, the calculation of specific surface areas would depend on the mean coverage per molecule or ion on the surfaces of the clay lattice. At maximum CPB adsorption, X-ray work by Greenland and Quirk¹³ showed that the hydrophobic cetyl chain projecting outwards at right angles from the clay surface and the mean coverage per CPB ion on a non-expanding clay lattice was 0.27 nm². In a similar study on methylene blue absorption, Pham and Brindley¹⁴ showed that the methylene blue molecules were lying flat on the clay mineral surfaces when optimum flocculation was reached. The effective area covered per methylene blue molecule under this condition was 1.30 nm². Despite the different orientations of the CPB ions and methylene blue

molecules on the clay surfaces, the specific surface areas of the various clay fractions determined by the two methods were almost similar. All indications are that these methods could be used for rapid measurement of specific areas of clay of Malaysian soils which consist predominantly of non-expanding lattices. Perhaps, the results of the procedures could be further clarified if parallel measurements of surface areas by the Brunauer, Emmett and Teller (B.E.T.) gas adsorption technique were made. In this instance, it is probable that the higher specific surface area of clay from Selangor series soil could be explained by the presence of both internal and external surfaces which could not be discriminately determined by the CPB and methylene blue absorption techniques alone. Therefore, for clay like that from Selangor series soil and the marine alluvial clay, the methylene blue and CPB techniques are not appropriate. For these categories of clay, the B.E.T. gas adsorption measurements will form the main core of future studies.

Correlation of Release and Adsorption of Cations in Soils

In earlier work, Lau² showed that the rates of release of potassium, magnesium and aluminium by five contrasting soils to a strong cation-exchange resin followed the 'first-order' rate law and the rates of adsorption of the same

cations from solution followed the 'parabolic' rate law. In this study, it was found that the rate constants for the release and adsorption of magnesium and aluminium were significantly correlated with the specific surface areas of the soils. The correlation coefficients and the regression equations are shown in Table 3. The good correlations between the rate constants for magnesium or aluminium release and surface areas suggested that the release is associated with the extent of the surface area of the soil for acid attack by the hydrogen ions from the cation-exchange resin. This observation agreed with the work of Ross¹⁵ who showed that acid dissolution of chlorites was influenced by the extent of the exposed surfaces of the clay mineral. Since aluminium and magnesium ions are strongly hydrated, the adsorption of these cations from solution would be strongly governed by the magnitude of the charges of the soil particles and total area of the exchange surface.

The higher specific surface areas of the Selangor and Durian clays allow for better retention of plant nutrients in the soils. However, advances in the agronomy research of rubber have shown that there were no correlations between uptake and yield of rubber and the nutrient retention capacity of the Selangor and Durian series soils as the overriding factor in these two soils are their serious

TABLE 3. LINEAR CORRELATIONS BETWEEN RATE CONSTANTS AND SPECIFIC SURFACE AREAS OF THE SOILS

Rate constant	Regression equation	Correlation coefficient (r)
First-order rate constants	$k_K = 2.046 + 0.003S$	0.053 ^{NS}
	$k_{Mg} = 0.445 + 0.014S$	0.743 ^{P<0.01}
	$k_{Al} = 8.453 + 0.062S$	0.600 ^{P<0.02}
Parabolic rate constants	$k_{K(p)} = 4.826 + 0.016S$	0.210 ^{NS}
	$k_{Mg(p)} = 2.872 + 0.018S$	0.852 ^{P<0.001}
	$k_{Al(p)} = 2.778 + 0.024S$	0.823 ^{P<0.001}

NS = Not significant

S = Specific surface area

k_K , k_{Mg} , k_{Al} are first-order rate constants;

$k_{K(p)}$, $k_{Mg(p)}$, $k_{Al(p)}$ are parabolic rate constants for K, Mg and Al respectively

soil physical limitations¹⁶. Rubber grown on Kuantan, Muchong and Rengam series soils generally have higher yield as the soils are better structured and root growth is not hampered. Conclusively, specific surface area measurement alone is insufficient and its influence on crop performance has to be considered together with other soil parameters.

CONCLUSION

The cetyl pyridinium bromide technique provides an alternate means for the rapid determination of specific surface areas of the highly leached and weathered inland soils of Malaysia. However, for marine alluvial soils which contain appreciable amounts of 2:1 expanding lattice minerals and organic matter, further clarification is required and parallel determination of specific surface areas using the B.E.T. gas adsorption method is necessary. The specific surface areas determined by the cetyl pyridinium bromide are comparable with those obtained from the amount of methylene blue absorbed by the soil from solution. The physico-chemical properties of the soils are influenced by the effective area of the exchanger.

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