

USE OF METHYLENE BLUE AND CRYSTAL VIOLET FOR DETERMINATION OF EXCHANGEABLE CATIONS IN MONTMORILLONITE

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Abstract—A procedure for the determination of cation exchange capacity (CEC) and the amounts of exchangeable cations adsorbed to montmorillonite is proposed. The method consists of a single incubation of the clay in a suspension containing a low concentration of an organic dye of large binding affinity, followed by analysis of the displaced inorganic cations by inductively-coupled plasma emission spectrometry (ICPES). The CEC is obtained by taking the largest sum of displaced exchangeable cations. Montmorillonite suspensions were incubated with methylene blue (MB) or crystal violet (CV) at dye concentrations below 4 mM, for one, three or fourteen days. For total dye concentrations up to the CEC, all the dye was adsorbed and equivalent amounts of exchangeable cations were released. Both dyes could adsorb to the clay in excess of the CEC.

After one day of incubation in the presence of dye concentrations of about 50% in excess of the CEC, the total amounts of cations released were reduced to below the CEC. This reduction was interpreted as due to massive aggregation of the clay particles induced by the dye. With CV the total amounts of cations released after three or fourteen days of incubation increased and became equal to the CEC.

The same CEC was found for Na-, Ca- and SWy1 crude-montmorillonite, by employing either of the dyes.

Key Words—Cation exchange capacity, Crystal violet, Exchangeable cations, ICP, Methylene blue, Montmorillonite, Organic cations.

INTRODUCTION

The amounts of exchangeable cations adsorbed to a clay are commonly determined by incubating the clay in a suspension containing a large concentration of a cation that is not included in the clay, such as NH_4^+ or Ba^{2+} , and then measuring the displaced cations by atomic absorption spectrometry (AAS) (Thomas, 1982). This procedure requires three or four incubations and separations, and there are several drawbacks: 1. Each application of the displacing cation requires a separation between the solution and the clay. Each separation results in loss of material. 2. The high concentration of the displacing solution may cause analytical disturbances during cation concentration measurements because of matrix and viscosity effects. Furthermore, measurements of AAS become problematic if the type of cations displaced is unknown. 3. Even three or four repetitions of the procedure may not be sufficient to displace all the exchangeable cations from the clay, e.g., Ca^{2+} from Ca-montmorillonite. Calculations in terms of an adsorption model (Nir, 1984; 1986) indicated that a complete removal of exchangeable cations cannot be achieved unless the displacing cation is of larger binding affinity to the clay than that of the initially adsorbed cations. The binding coeffi-

cients (M^{-1}) to montmorillonite of Li^+ , Na^+ , K^+ , Cs^+ (Nir *et al.*, 1986) and Cd^{2+} (Hirsch *et al.*, 1989) are 0.6, 1, 2, 200 and 10, respectively. Preliminary work (Rytwo, Nir and Banin, unpublished) indicates that the binding coefficients for Ca^{2+} and Mg^{2+} may be at least $5\text{--}10 M^{-1}$. It has not been shown that the binding affinities to montmorillonite of other inorganic cations such as NH_4^+ or Ba^{2+} are extremely large. On the other hand, organic cations have been found to adsorb strongly to clays (Chu and Johnson, 1979; De *et al.*, 1974; Ghosal and Mukherjee, 1972; Grauer *et al.*, 1984; Lagaly, 1984; Mortland, 1970; Narine and Guy, 1981; Raussel-Colom and Serratos, 1987; Theng, 1974; Venugopal and Nair, 1974). The organic cations methylene blue (MB) and thioflavin T (TFT) were previously shown to have binding coefficients of at least 10^8 and $10^9 M^{-1}$ (Margulies *et al.*, 1988). While Cs^+ is of a much higher affinity to montmorillonite than Na^+ or K^+ , the adsorption isotherm of TFT with dye concentrations lower than the cation exchange capacity (CEC) was practically the same in the presence of $<10 \text{ mM Na}^+$ or 3.5 M Cs^+ .

In this work, we propose to determine the amounts of adsorbed inorganic cations, as well as the CEC of clays. We employ low solution concentrations of the organic cations (dyes) MB and CV (Figure 1), combined with inductively-coupled plasma emission spectrometry (ICPES). We illustrate the application of the proposed procedure to Na-, Ca- and SWy1 crude-mont-

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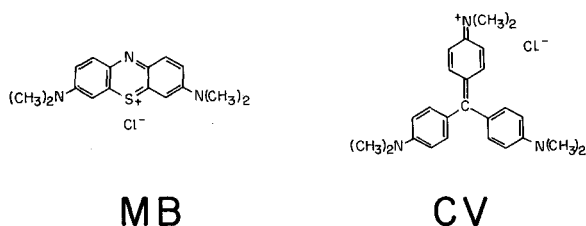


Figure 1. Molecular structures of methylene blue (MB) and crystal violet (CV).

morillonite and discuss how to avoid a problem that can arise if relatively large concentrations of the dyes are applied.

EXPERIMENTAL

Materials

Wyoming Na-montmorillonite SWy-1 was obtained from the Source Clays Repository of The Clay Minerals Society. Methylene blue and crystal violet were obtained as chloride salts from Merck and from Fluka Chemica, respectively, and were used without further purification. Analytical reagents NaCl (BDH) and CaCl₂ (Merck) were used to prepare homoionic clays.

Homoionic clays

Homoionic Na- and Ca-montmorillonite were prepared from the SWy-1 clay using a batch procedure. A suspension of clay in the corresponding 1 N salt solution was shaken for 24 hours at 25°C. The equilibrated solution was separated from the clay by centrifugation (30 minutes at 14,000 rpm) in a Kontron Centrikon H-401 centrifuge. This procedure was repeated three times for the Ca-clay, and four times for the Na-clay. The precipitate was washed three times with distilled water and freeze-dried in a Christ Alpha 1-4 lyophilizer.

Adsorption/desorption isotherms

To measure the adsorption isotherms of the two dyes and the desorption of the inorganic cations from the clays, aliquots of an aqueous 1×10^{-2} M solution of dye were added dropwise, under continuous stirring, to 20 ml of a 0.5% w/w clay suspension in 100 ml polyethylene bottles. The final volume was brought to 60 ml. The bottles were sealed, kept at $25 \pm 2^\circ\text{C}$, and had continuous agitation applied. After incubation times of 1, 3 or 14 days, 10 ml of suspension were taken from each bottle and filtered through S&S FP030/2 (0.45 μm) filters. The concentration of the dye in the filtrates was determined by measuring the absorption at 662 nm (MB, $\epsilon = 61,000 \text{ M}^{-1}\text{cm}^{-1}$) and at 588 nm (CV, $\epsilon = 83,000 \text{ M}^{-1}\text{cm}^{-1}$), using a HP 8452A diode array UV-Vis spectrophotometer.

Concentrations of inorganic cations in solution were determined using a Spectra ICP emission spectrometer,

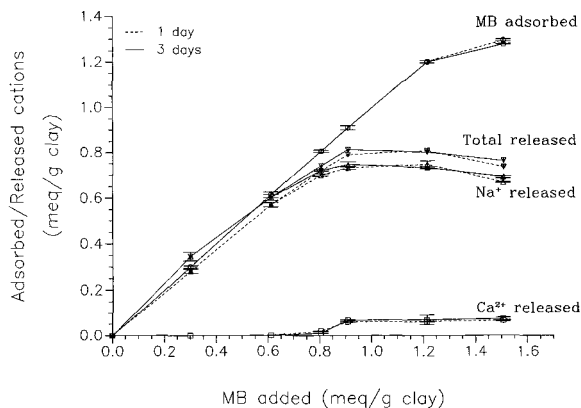


Figure 2. Adsorption of methylene blue (MB) and desorption of inorganic cations from Na-montmorillonite after 1 and 3 days of incubation.

and amounts of cations released were calculated. Dye solutions and filtrates from suspensions of clays in distilled water were used as blanks. ICPEs measurements of standards for inorganic cations dissolved in dye solutions of different concentrations showed that the presence of the organic dyes did not interfere with the analysis of the inorganic ions.

Experiments were carried out in triplicate. Since the concentrations of added dyes were in the range 0–1.5 meq/g clay, the highest concentration of dye in the solutions was lower than 4×10^{-3} M.

RESULTS

Methylene blue

Figures 2–4 show adsorption/desorption isotherms of MB to Na-montmorillonite, Ca-montmorillonite and SWy-1 crude after one and three days of incubation. The amounts of released cations and adsorbed dye after fourteen days of incubation (not shown) were very similar to those following three days of incubation. The differences between one and three days were small.

When small amounts of MB were added (up to 0.8 meq/g clay) all the dye was adsorbed. Dye concentrations in the filtrates were lower than the instrumental limit of detection (10^{-7} M). In the Na-clay (Figure 2) complete dye adsorption continues up to 1.2 meq/g clay, whereas in the Ca-clay (Figure 3) saturation occurs at 0.9 meq/g clay. At these added concentrations, the amounts of desorbed cations found for the three clay treatments were almost identical (0.8 meq/g clay). At higher dye concentrations, the amount of desorbed cations decreased. This decline is more significant for the Ca-clay.

The results in Figure 2 illustrate the difficulty in preparing a homoionic Na-montmorillonite, as explained in the introduction. Also it is observed that Ca²⁺ is released to the solution only after almost all the Na⁺ is displaced. This is explained by the difference

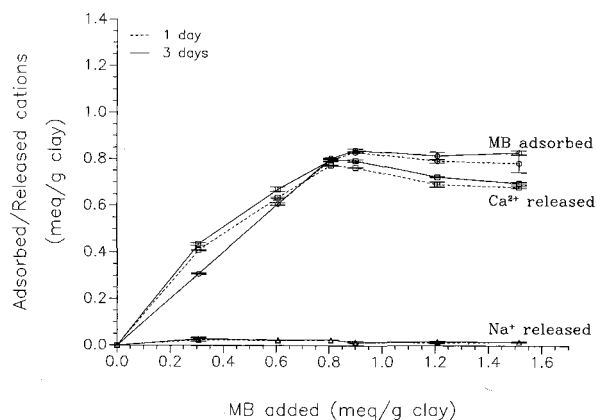


Figure 3. Adsorption of methylene blue (MB) and desorption of inorganic cations from Ca-montmorillonite after 1 and 3 days of incubation.

in valency and binding affinity for these two cations. Figure 4 shows that SWy-1, which is distributed as Na-montmorillonite, still contains large amounts of divalent cations (van Olphen and Fripiat, 1979). An earlier release of Na^+ can be observed here, as in Figure 2.

Crystal violet

Figures 5–7 present adsorption/desorption isotherms of CV to Na-montmorillonite, Ca-montmorillonite and SWy-1 crude after one and three days of incubation. As with MB, the amounts of cations released after two weeks or three days of incubation were very similar, but the amounts of dye adsorbed were slightly higher after two weeks.

For the Na-clay (Figure 5), most of the dye is adsorbed up to 1.5 meq/g clay. For SWy-1 (Figure 7), all the dye is adsorbed up to added CV amounts of 1.2 meq/g clay, while in the Ca-clay (Figure 6) the limit was 0.9 meq/g clay. As with MB, when added amounts

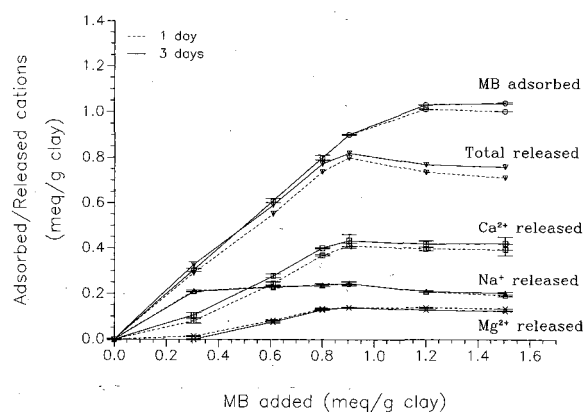


Figure 4. Adsorption of methylene blue (MB) and desorption of inorganic cations from SWy-1 montmorillonite after 1 and 3 days of incubation.

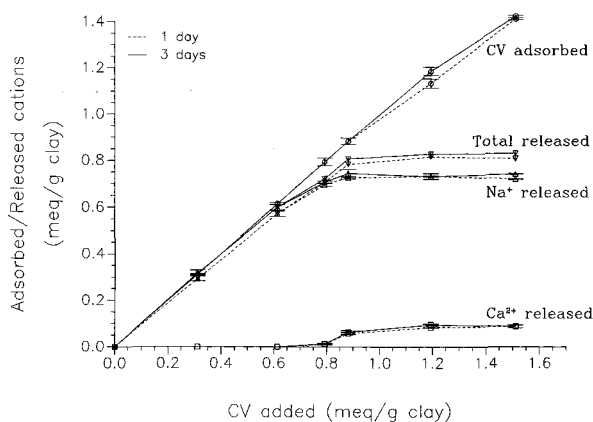


Figure 5. Adsorption of crystal violet (CV) and desorption of inorganic cations from Na-montmorillonite after 1 and 3 days of incubation.

of CV were 0.9 meq/g clay, the total amount of cations released was 0.8 meq/g clay. However, the effect described with higher MB concentrations, i.e., a decrease in the amounts of cations released, was not observed for CV after 3 days of incubation. An increase in the Ca^{2+} contents in the clay resulted in prolonged times required for completion of the adsorption of CV (Figures 5–7). In the Na-clay dye adsorption was completed in one day (Figure 5), whereas in the Ca-clay (Figure 6) it took more than three days.

DISCUSSION

The application of MB and CV dyes to montmorillonite suspensions yields similar amounts of cations released. This can be seen by comparing Figures 2 and 5 (Na-clay), 3 and 6 (Ca-clay) and 4 and 7 (SWy-1 crude). Such similarity proves that both dyes displace all the exchangeable cations when the amount of dye added is slightly above the CEC. Figure 8 combines

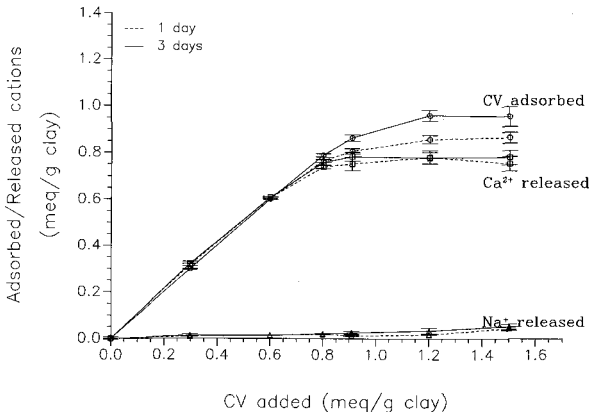


Figure 6. Adsorption of crystal violet (CV) and desorption of inorganic cations from Ca-montmorillonite after 1 and 3 days of incubation.

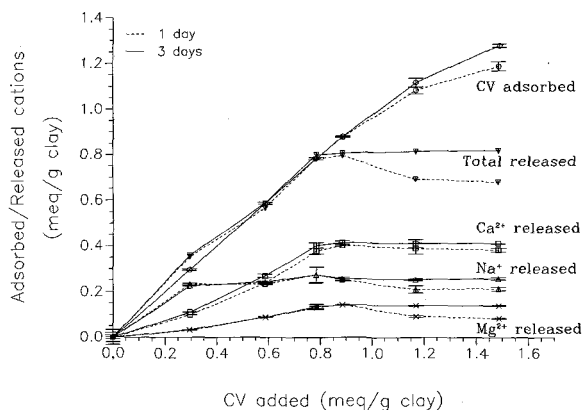


Figure 7. Adsorption of crystal violet (CV) and desorption of inorganic cations from SWy-1 montmorillonite after 1 and 3 days of incubation.

the results for the three clays, after three days of incubation, and for two dye concentrations. One is slightly above CEC (0.9 meq/g clay), and the other almost twice the CEC (1.5 meq/g clay). At higher amounts of added MB, the dye does not displace all the inorganic cations. We suggest that with high added concentrations of MB, clay aggregates are formed and coated with dye. The coating prevents the penetration of MB molecules into the space between the clay particles. With CV this effect is smaller (Figure 7). Aggregates of clay particles may also be formed, but after three days CV molecules manage to penetrate into the aggregates, and displace the inorganic cations.

Although a reasonable CEC value can be calculated from the sum of the released inorganic cations, it cannot be reliably determined from the amounts of dyes adsorbed (Hang and Brindley, 1970). For both the MB and CV dyes, more is adsorbed by the Na- than by the Ca-treated clay, with the SWy-1 being intermediate. A larger amount of Na^+ in the clay, at the expense of Ca^{2+} , results in a more dispersed clay, which in turn enhances the amounts of dye adsorbed.

Figure 8 shows that the two dyes yield the same CEC for the three clay treatments employed. This result can be explained by the fact that the homoionic clays were prepared from SWy-1.

CONCLUSIONS

A combination of either methylene blue or crystal violet with ICPEs technology can be used as an accurate and efficient procedure for determining the composition of exchangeable cations and CEC in montmorillonite.

The use of one of these organic cations avoids the need for several incubations and separations with high concentrations of displacing solutions. The use of ICPEs improves the accuracy of the measurements, and en-

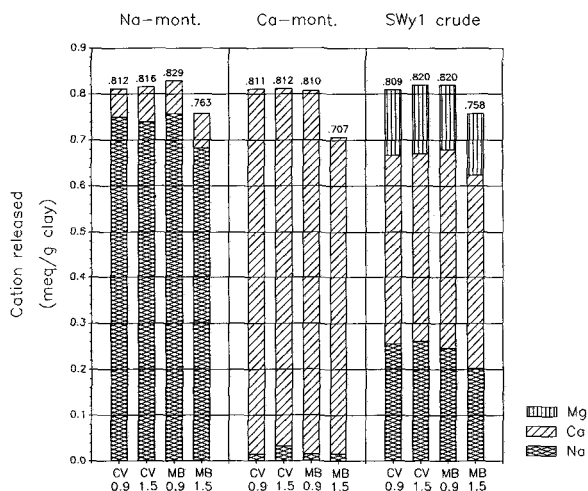


Figure 8. Inorganic cation released from the montmorillonite clays by crystal violet (CV) and methylene blue (MB) at added concentrations of 0.9 and 1.5 meq dye/g clay. Sum of cations released appears above each column.

ables the amounts of several cations to be measured simultaneously.

An incubation time of three days was sufficient for the clays studied. If an appropriate dye concentration is used (0.9–1.0 meq/g clay) the difference between one and three days is not significant.

Of the two dyes studied, CV might be preferred, due to the absence of incomplete displacement of adsorbed inorganic cations that appears with high MB concentrations. Even so, if the CEC of a clay is approximately known (or estimated in a preliminary experiment), MB can be applied at concentrations slightly above CEC. The employment of MB has the advantage of a low level of impurities.

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