

## EVIDENCE OF DEGRADATION OF TRIARYLMETHINE DYES ON TEXAS VERMICULITE

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**Abstract**—Synthetic dyes in industrial effluents pose a significant risk to human health and the environment, so much effort has been expended to degrade them using various methods, including the use of clay minerals as catalysts. The purpose of this study was to advance understanding of the mechanisms for clay-catalyzed degradation of crystal violet (CV) and other triarylmethine dyes using three different vermiculite clays (Llano, Texas, VTx-1; Ojen, OV; and Russian, RV), a montmorillonite (SWy-1), and a Spanish sepiolite (SEP). While OV, RV, SWy-1, and SEP showed almost no activity with respect to dye degradation, VTx-1 caused complete removal of the dye from solution up to the equivalent of 200% of the cation exchange capacity of the clay. While large amounts of dye were removed from the solution, no change in basal spacing was observed by X-ray diffraction. The kinetics of removal of CV from solution began after a lag period of >10 days in a process that can be described by pseudo-second order kinetics. By comparison, adsorption of CV onto SWy-1 and SEP was immediate, without any lag period. Sonication treatment of the VTx-1 vermiculite suspension caused the CV removal process to begin immediately. Fourier-transform infrared measurements of adsorption of CV on clays revealed that for the OV and RV vermiculites, SEP sepiolite, and SWy-1 montmorillonite the spectra were similar to the original dye; the spectra of the VTx-1-dye differed considerably, however, exhibiting vibrations of methylene groups ( $-\text{CH}_2-$ ) which were not present in the CV molecule. The significant changes in the IR spectrum indicated that CV underwent degradation on the surface of the VTx-1 vermiculite. Carbon-content analysis led to the conclusion that degradation products remained bound to the clay. Similar effects were observed for two other triarylmethine dyes (malachite green and methyl green) added to VTx-1, indicated that it may, therefore, be considered suitable as a sorbent to remove and decompose such dyes from industrial effluents. Pretreatment by sonication would remove the need for long incubation times.

**Key Words**—Arnolds Base, Crystal Violet, FTIR, Vermiculite, Adsorption, Degradation, Pseudo-second Order Kinetics.

Abbreviations: Arnolds base (4,4'-Methylenebis(*N,N*-dimethylaniline)); BG, brilliant green ([4-[(4-diethylaminophenyl)-phenylmethylidene]-1-cyclohexa-2,5-dienylidene]-diethylazanium); CEC, cation exchange capacity; crude VTx-1, untreated Llano Texas vermiculite; CV, crystal violet (4-[[4-(dimethyl aminophenyl)-methylidene]-1-cyclohexa-2,5-dienylidene]-dimethylazanium); FTIR, Fourier-transform infrared; MG, methyl green (4-[[4-(Dimethylamino) phenyl][4-(dimethylimino)-2,5-cyclohexadien-1-ylidene]methyl]-*N*-ethyl-*N,N*-dimethylbenzenaminium); OV, Ojen vermiculite; RV, Russian vermiculite; SEP, Spanish sepiolite; SWy-1, Wyoming SWy-1 montmorillonite; UV-Vis, ultraviolet and visible; VTx-1, Llano, Texas vermiculite; XRD, X-ray diffraction.

### INTRODUCTION

Synthetic dyes are widely used in the paper, plastic, textile, leather, and printing industries (Alshamsi *et al.*,

2007; Zollinger, 2003). Triarylmethine dyes are among the most frequently used dyes, and only azo-dyes are more abundant. About 15% of the dyes produced are lost to wastewater during synthesis or while processing (Gupta *et al.*, 2006). As most dyes are harmful, effluents from such industries pose environmental hazards to human and aquatic life (Alshamsi *et al.*, 2007; Boeningo, 1994). Efficient degradation of such dyes is, therefore, of broad environmental interest in order to avoid pollution of water sources.

Conversion of organic dye effluents to harmless compounds has been attempted by various methods including flocculation, adsorption, chemical oxidation, and even photocatalytic degradation on TiO<sub>2</sub> surfaces (Li *et al.*, 1999; Wang, 2000; Sahoo *et al.*, 2005).

Clay minerals are known as efficient and environmentally benign catalysts for organic reactions in nature and industry. The catalytic potential of clays is ascribed to the specific structural properties of the minerals which can act either as Brønsted or as Lewis acids, and to their large surface areas available for liquid-phase reactions (Adams and McCabe, 2006).

Vermiculites are 2:1 layered phyllosilicates, with a large negative layer charge which originates from

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isomorphic substitutions in the tetrahedral sheet of the mineral. Organic compounds interact strongly with the oxygen plane of the platelets, and the interactions are stronger for organic cations. Due to the "relatively large charge density", the interlayer inorganic cations in vermiculites are more difficult to exchange and are less mobile (Perez-Rodriguez and Perez-Maude, 2002). Therefore, the amounts of organic cations sorbing to vermiculite are assumed to be considerably smaller than those observed for montmorillonite or smectite. In some cases (De *et al.*, 1979), maximum adsorption of CV onto vermiculite was only 20% of the cation exchange capacity (CEC), while for smectite it reached 180% of the CEC (Rytwo *et al.*, 1995) and >300% of the CEC on sepiolite (Rytwo *et al.* 1998).

In the present study, the adsorption behavior of the triarylmethine dye crystal violet (CV) was tested on three vermiculites: Ojen vermiculite (OV), Russian vermiculite (RV), and Llano, Texas, vermiculite (VTx-1). The kinetics of dye removal from solution were compared with two other clays (Spanish sepiolite and SWy-1 montmorillonite). UV-Vis measurements showed no aggregation whereas FTIR spectra of organo-clay complexes revealed evidence of degradation of CV and two additional triarylmethine dyes (brilliant green (BG) and methyl green (MG)) by VTx-1.

## MATERIALS AND METHODS

Ojen vermiculite (OV) with a CEC of  $1.43 \text{ mol}_c\text{kg}^{-1}$  (Jimenez de Haro *et al.*, 2005) was obtained from CSIC-Sevilla. Russian MX-80 vermiculite (RV) was obtained from Thermax, Austria, with a CEC of  $1.62 \text{ mol}_c\text{kg}^{-1}$  (Dultz *et al.* 2005). Llano, Texas, VTx-1 vermiculite was supplied by Prof. Arieh Singer. The dominant exchangeable cation was  $\text{Mg}^{2+}$ , and the reported CEC was  $2.1 \text{ mol}_c\text{kg}^{-1}$  (Eick *et al.*, 1990). SWy-1 montmorillonite, with a CEC of  $0.764 \text{ mol}_c\text{kg}^{-1}$  (van Olphen and Fripiat, 1979), was obtained from The Clay Minerals Society's Source Clays Repository (Purdue University, Lafayette, Indiana). Spanish sepiolite, with a CEC of  $0.15 \text{ mol}_c\text{kg}^{-1}$  (Ruiz-Hitzky and Casal, 1985), was supplied by Tolsa, S.A. (Madrid, Spain). In all minerals only the clay-size fraction prepared by sedimentation ( $<2 \mu\text{m}$ ) was used. The CV, BG, and MG were purchased from Fluka Chemie, and Arnolds base was purchased from Sigma-Aldrich. All materials were used without further purification.

For adsorption experiments of CV on the vermiculite clays, 1% dispersions of each were prepared by adding the clay gradually to distilled water while stirring. Appropriate amounts of CV were added to achieve amounts equivalent to 20%, 50%, 100%, and 150% of the CEC of each clay. Bottles were kept agitated at  $25 \pm 0.5^\circ\text{C}$ . After 2 weeks, 10 mL was removed and centrifuged using a C-3000 Jouan centrifuge at 2500 rpm for 30 min. The concentration of CV in the supernatant was determined by UV-Vis spectroscopy

using a diode array HP 8452A spectrophotometer, at 588 nm. All experiments were executed in triplicate.

As no significant adsorption was observed for either the OV or RV samples, further detailed adsorption and kinetics experiments were carried out only with VTx-1. A 1% VTx-1 suspension was prepared and treated with an ultrasonic needle for 10 min. The ultrasonic treatment was performed using a W-375 Heat System Ultrasonic liquid processor with 600 W output, a 20 kHz convertor, and a titanium disruptor 12.7 mm diameter horn, with a radiating tip of 120  $\mu\text{m}$ . The horn tip was dipped into a cylindrical jacketed cooling cell of 5 cm internal diameter, where the dispersion was placed. The temperature of the instrument was kept constant at  $25^\circ\text{C}$  during the treatment. 4 mL of sonicated clay suspension was added to the CV solution, achieving a total volume of 40 mL. The final clay concentration was  $1 \text{ g L}^{-1}$ , and the concentrations of CV added ranged from 0.6 to 3.6 mM (equivalent to 29–171% of the CEC). The bottles were agitated constantly at  $25 \pm 0.5^\circ\text{C}$ . After 1, 3, 7, 10, and 15 days, 6 mL was removed from each bottle, centrifuged, and the remaining CV concentration in solution was measured as described above. The amounts of dye removed from the solution were calculated from mass balance. After separation of the supernatant, the precipitate was dried in a desiccator over silica gel and used afterwards for FTIR, XRD, and CHNSO (carbon, hydrogen, nitrogen, sulfur, and oxygen) measurements. Additional samples of SWy-1 and SEP with CV added at 100% of the CEC of each clay mineral (*i.e.* 0.14 and 0.78  $\text{mol}_c\text{kg}^{-1}$  for SEP and SWy-1, respectively) were similarly prepared. From the bottles with CV added at 100% of the CEC prepared for the FTIR measurements, UV-Vis spectra of unfiltered suspensions of CV-SWy-1, CV-SEP, and CV-VTx-1 clay complexes were measured and compared with the spectra of free CV in solution. The amount of dye adsorbed was calculated as in the adsorption experiments. The CV concentration in solution with all three clays was less than the limit of detection, indicating complete adsorption. Similar results were reported for SWy-1 and SEP in previous studies (Rytwo *et al.*, 1995, 1998). Suspensions from the crude clays were measured similarly, but no significant optical absorption was observed above 400 nm.

Comparative kinetic adsorption experiments were performed by adding CV solution to glass bottles containing stirred suspensions of 0.1 g/L SWy-1, SEP, or VTx-1. The initial CV concentration was 150% of the CEC of the respective clays (*i.e.* 21, 120, and 315  $\mu\text{M}$  for SEP, SWy-1, and VTx-1, respectively). The CV concentration in the bottles was measured several times by removing 5 mL of each clay suspension, filtering it using 0.45  $\mu\text{m}$  syringe filters, and measuring the UV-visible spectra using a diode array HP 8452A, as described above.

The concentrations of organic compounds bound to VTx-1 were calculated from combustion elemental analysis (CHNSO) measurements, performed using a

Thermo Elemental Analyzer 1108, which reported the C content of the sample. All surplus C, compared with the clay to which no CV was added, was attributed to CV.

In order to further study interactions between CV and the clay, FTIR spectra of dried organo-clay complexes were recorded from KBr pellets. Spectra of analytical CV and Arnolds base were recorded in similar fashion. All measurements were performed using a Magna-IR 550 FTIR spectrophotometer (Nicolet Analytical Instruments, Madison, Wisconsin), and analyzed with OMNIC software. The FTIR spectra of BG and MG on VTx-1 clay, and the spectra of all three triarylmethine dyes added to OV, RV, SWy-1, and SEP at 100% of the CEC of each clay were performed in the same way.

The basal spacing values of untreated (no CV added) and 100% CEC CV-treated (*i.e.* 2.1 mol<sub>c</sub>/kg) VTx-1 vermiculite were measured by XRD by placing a few drops of each dispersion on glass microscope slides and allowing them to air dry for 7 days. Measurements were performed using a Philips PW1830/3710/3020 diffractometer with a CuK $\alpha$  radiation source ( $\lambda = 1.544 \text{ \AA}$ ) in the range  $2-10^\circ 2\theta$  at a scanning rate of a  $1^\circ/\text{min}$ .

## RESULTS AND DISCUSSION

### Removal of CV from equilibrium solution by sonicated VTx-1

The preliminary experiments with CV added in amounts equivalent to 20, 50, 100, and 150% of the CEC to all three clays showed that for samples OV and RV the CV concentration remained almost unchanged (<2% variation) after 2 weeks, indicating very low adsorption or degradation of the dye. On the other hand, the supernatant of samples with VTx-1 clay were almost clear, indicating that most dye had been removed from solution, even at large dye concentrations.

In order to further understand the process, a detailed adsorption experiment on sonicated VTx-1 was performed, focusing on the depletion of CV from solution. Apparent adsorption isotherms of CV on VTx-1 at various equilibration times (see Figure 1) show that, after 1 day, removal from solution reached only ~50% of the CEC (*i.e.* 1.0 mol<sub>c</sub>/kg). After 3 days, amounts removed increased to 100% of the CEC of the clay (~2.1 mol<sub>c</sub>/kg), and after 2 weeks the amounts removed were >150% of the CEC (*i.e.* >3.3 mol<sub>c</sub>/kg). Thus, when the clay was sonicated, a decrease in CV solution concentration began immediately and the removal from the solution was relatively fast, as observed, in particular, at low concentrations added.

### Comparative kinetics of the removal of CV from solution by three un-sonicated clay minerals

In order to compare sorption kinetics, adsorption of CV on SEP, SWy-1, and VTx-1 added in amounts equivalent to 150% of the CEC of each clay (*i.e.* 0.21, 1.20, and 3.15 mol<sub>c</sub>/kg, respectively) was measured after reaction times ranging from 300 to 40,000 min (up to ~28 days). As mentioned in the experimental section, all clay minerals were prepared as a  $0.1 \text{ g L}^{-1}$  suspension, without sonication. The amounts removed from solution were considered to have been adsorbed and the results were consistent with a pseudo-second order model using equation 1 (Ho and McKay, 2000; Aksu and Kabasakal, 2004):

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e}t \quad (1)$$

where  $t$  is the time (min),  $q_e$  and  $q_t$  are the equilibrium amount sorbed and the amount sorbed at time  $t$ , respectively ( $\text{g}_{\text{CV}} \text{ kg}_{\text{clay}}^{-1}$ ), and  $k$  is the rate constant of sorption (Ho and McKay, 2000) [ $\text{kg}_{\text{clay}} \text{ g}_{\text{CV}}^{-1} \text{ min}^{-1}$ ]. Even

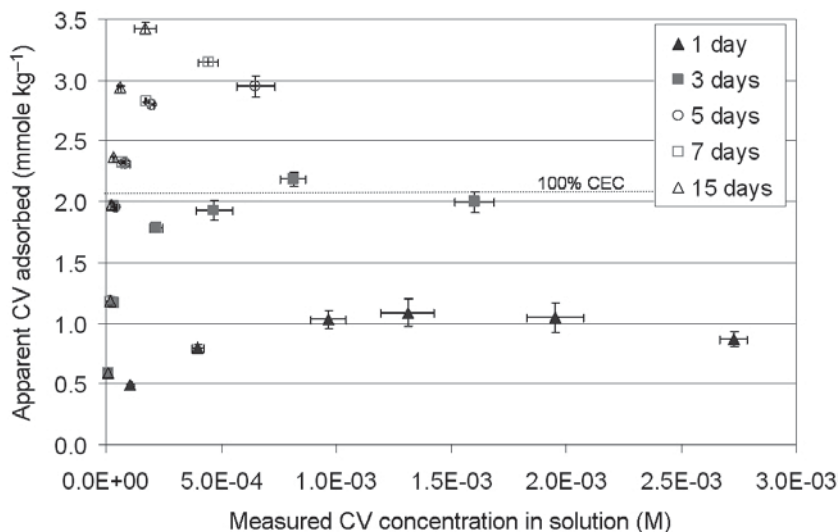


Figure 1. Adsorption isotherms of CV on sonicated VTx-1 after 1, 3, 5, 7, and 15 days.

Table 1. Rate constant of sorption ( $k$ ), equilibrium amount sorbed ( $q_e$ ), and the determination coefficient ( $R^2$ ) for the kinetics of CV sorbing to clays, based on the pseudo-second order model.

Remarks	SD	$R^2$	$q_e$ ( $\text{g}_{\text{CV}} \text{kg}_{\text{clay}}^{-1}$ ) (% CEC)	$k$ ( $\text{kg}_{\text{clay}} \text{g}_{\text{CV}}^{-1} \text{min}^{-1}$ )	Clay
	9.06%	0.9963	60.3 (116%)	2.98E-05	Spanish sepiolite (SEP)
	2.37%	0.9999	378.5 (127%)	3.00E-04	SWy-1 montmorillonite
Not sonicated, all data	54.45%	0.0201	5038.3 (643%)	7.60E-10	VTx-1 vermiculite
Not sonicated, only data starting at $t = 16,000$ min	7.74%	0.9737	1147.4 (146%)	2.70E-07	
Sonicated	8.34%	0.9954	1236.2 (156%)	3.68E-07	

though the pseudo-second order equation is empirical and cannot give information about the sorption mechanism (Gonen and Rytwo, 2007), it has been applied successfully to the adsorption of metal ions, dyes, herbicides, oils, and organic substances from aqueous solutions (Ho, 2006). Table 1 summarizes the values for the rate constant of sorption ( $k$ ) and equilibrium amount sorbed ( $q_e$ ), including the determination coefficient ( $R^2$ ), and standard deviation between the calculated and measured values (SD), which are considered to be parameters indicating the fitness of the model to the experimental results (Chang and Juang, 2004).

From equation 1, one can deduce that when the process fits the pseudo-second order equation, lines plotting the ratio  $t/q_t$  as a function of time should yield linear fits. Such highly correlated linear fits were indeed measured (Figure 2) for SEP (filled triangles) and SWy-1 (filled squares). In fact, for both of these clays,

the removal process was almost complete within a matter of minutes. In the case of un-sonicated vermiculite (open rhombus), however, no linearity was observed. Even though this point is not explicit in the format chosen for Figure 2, which focuses on the pseudo-second order model, the CV concentration stayed almost constant for  $\sim 11$  days. After this time a decrease in the concentration of the dye appeared, and only 13% of the initial dye remained in solution after 28 days (40,000 min). Analyzing the data of the vermiculite experiment starting after 16,000 minutes ( $\sim 11$  days, filled rhombus) revealed a clear linearity in the pseudo-second order plot (Figure 2), with large  $R^2$  ( $>0.97$ ) and small SD values ( $<8\%$ ), indicating a good fit to the model (Table 1). An interesting comparison of the kinetics of un-sonicated and sonicated vermiculite (asterisks) was obtained from the data presented in Figure 1 for the experiment with CV added at 150% of

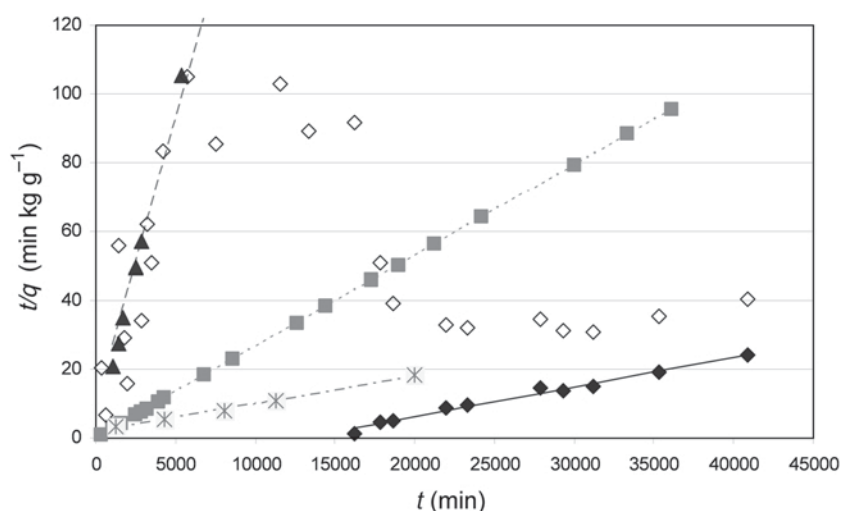


Figure 2. Plots of pseudo-second order kinetic model for adsorption of CV on SEP (triangles, dashed line), SWy-1 (squares, dotted line), and VTx-1 (rhombus, full line). Points represent measured values, and lines are calculated values using a pseudo-second order model (equation 1) and coefficients from Table 1. The open rhombus represents VTx-1 results along the full time scale, whereas the filled rhombus represents VTx-1 results starting from  $t = 16,000$  min. Asterisk points and dot-dashed lines represent measured and calculated values for sonicated clay added under the same experimental conditions (adapted from data in Figure 1).

the CEC. The equilibrium amounts sorbed ( $q_e$ ) and the rate constant of sorption ( $k$ ) of the sonicated vermiculite and the un-sonicated vermiculite as calculated after 16,000 min (last two rows at Table 1) are indeed of the same respective order of magnitude. The results suggest that sonication of the vermiculite caused the process to start immediately, but for un-sonicated vermiculite, >10 days were needed for the opening of the tactoids and initiation of the process. Previous studies had shown that sonication of vermiculite induced delamination and reduction of the particle size, without changing the chemical constitution of the minerals (Jimenez de Haro *et al.*, 2005). According to the results presented in Table 1 and Figure 2, such delamination allowed immediate reaction without the need for a lag stage, yielding similar kinetic parameters ( $k$  and  $q_e$ ) as for un-sonicated clay after a lag stage of 11 days.

#### XRD and CHNSO measurements

With a working assumption that the large amounts of CV removed from the solution were adsorbed to VTx-1 clay, samples of the experiment presented in Figure 1 were used to measure the basal spacings of the platelets without dye and with dye added (and removed from solution) up to 100% of the CEC. In previous studies (Ramirez-Valle, Huterer-Shveky, and Rytwo, 2005, unpublished results) the basal spacing of OV intercalated with methylene blue increased from 1.42 to 2.00 nm. Similar changes in basal spacing were reported for adsorption of CV on smectite (Rytwo *et al.*, 1995), where the configuration of CV molecules on the clay platelet was oblique, with strong CV-CV interactions and relatively weak CV-clay interactions. However, in this case, XRD patterns of the crude VTx-1 without and with 100% CV added (*i.e.* 2.1 mol<sub>c</sub>/kg, results not shown) exhibited sharp peaks at  $6.10^\circ 2\theta$  (~1.45 nm), identical for both samples. Thus, removal of large amounts of CV from solution failed to cause an increase in the basal spacing.

The CHNSO measurement of the precipitate in tubes containing VTx-1 with CV added in an amount equivalent to up to 100% of the CEC was performed. The C content was used to evaluate the amount of CV bound to the clay platelets, yielding an equivalent of 104.6% of the CEC (2.1 mol<sub>c</sub> CV kg<sup>-1</sup> clay). Thus, the results confirmed that at least the original amount of organic C remained attached to the surface of the clay, even though the basal spacing remained unchanged.

#### FTIR analysis

The vibrational spectrum of a molecule is considered to be a unique physical property characteristic of the molecule. As such, it can be used as a fingerprint for identification by comparing results with reference spectra. In the absence of a suitable reference database, a basic interpretation of the spectrum can still be performed from first principles, leading to characteriza-

tion and possibly even identification of an unknown sample (Coates, 2000). In order to study the interactions between the CV molecules and vermiculite, FTIR measurements of spectra of CV equivalent to 100% of the CEC adhering to several clays were performed. Spectra of pure CV and of Arnolds base (see Figure 4 for the chemical structures of organic compounds) were measured for comparison. The range between 1100 and 1700 cm<sup>-1</sup> (Figure 3) demonstrated that spectra of CV adsorbed on RV, OV, SWy-1, and SEP clays are similar to pure CV, while CV adsorbed on VTx-1 was very different from the others and showed strong similarity to the Arnolds base spectrum. Table 2 lists the assignments of the IR vibrations on the different samples. The peaks at ~650 cm<sup>-1</sup> are assigned to Si-O vibrations of the various clay minerals (Madejová and Komadel, 2001). Additional clay vibrations appeared at 990–1050 cm<sup>-1</sup> (Si-O in-plane stretching) and accompanied by longitudinal vibrations (shoulders in the 1060–1120 cm<sup>-1</sup> range). Structural OH-stretching modes were observed in all organo-clays at 3400–3600 cm<sup>-1</sup>, though OH vibrations ascribed to sorbed water (1650 cm<sup>-1</sup>) appeared only when the amounts of CV adsorbed were small (CV-OV, CV-RV) or in SEP, where zeolitic water is expected (CV-SEP 1665 and 3387 cm<sup>-1</sup>). For CV-VTx-1 and CV-SWy-1, no adsorbed water was observed, indicating dehydration by the large amounts of bound organic compounds.

In the range 650–900 cm<sup>-1</sup> (Figure 3), several out-of-plane C-H ring vibrations were observed (Coates, 2000). While the peaks at 800–850 cm<sup>-1</sup> are ascribed to 1,4 aromatic di-substitution (para), present in both pure CV and Arnolds base molecules, the peak at ~721 cm<sup>-1</sup> generally indicates mono-substitution. However, it could also occur in several other cases with di-substitutions (Williams and Fleming, 1989), and in this case can be correlated to the amount of CV adsorbed onto the organo-clay. On CV-SWy-1 the peak was strong; on CV-OV and CV-RV it was very weak, due to the small amounts of dye adsorbed. In CV-SEP, the peak was also relatively small, as the CEC of SEP was ~20% of the CEC of SWy-1 montmorillonite. One should note that for the CV-VTx-1 sample, this peak was almost absent, even though all CV dye was removed from solution due (presumably) to its sorption onto the clay. Interestingly, this peak is also completely absent from the FTIR spectra of possible CV decomposition products such as Arnolds base or Michler's hydrol, indicating that the adsorbed organic compound on VTx-1 was not CV. The details of all the FTIR spectra in Figure 3 are listed in Table 2, along with the spectrum of crude sonicated VTx-1. Results of the latter are almost identical to those shown in previous studies (Schosseler and Gehring, 1996). The spectrum showed a band at 1639 cm<sup>-1</sup> which can be attributed to molecular vibration of water. The weak 1441 cm<sup>-1</sup> band is typical of the asymmetric stretching vibration of CO<sub>3</sub><sup>2-</sup> for carbonates (MgCO<sub>3</sub>,

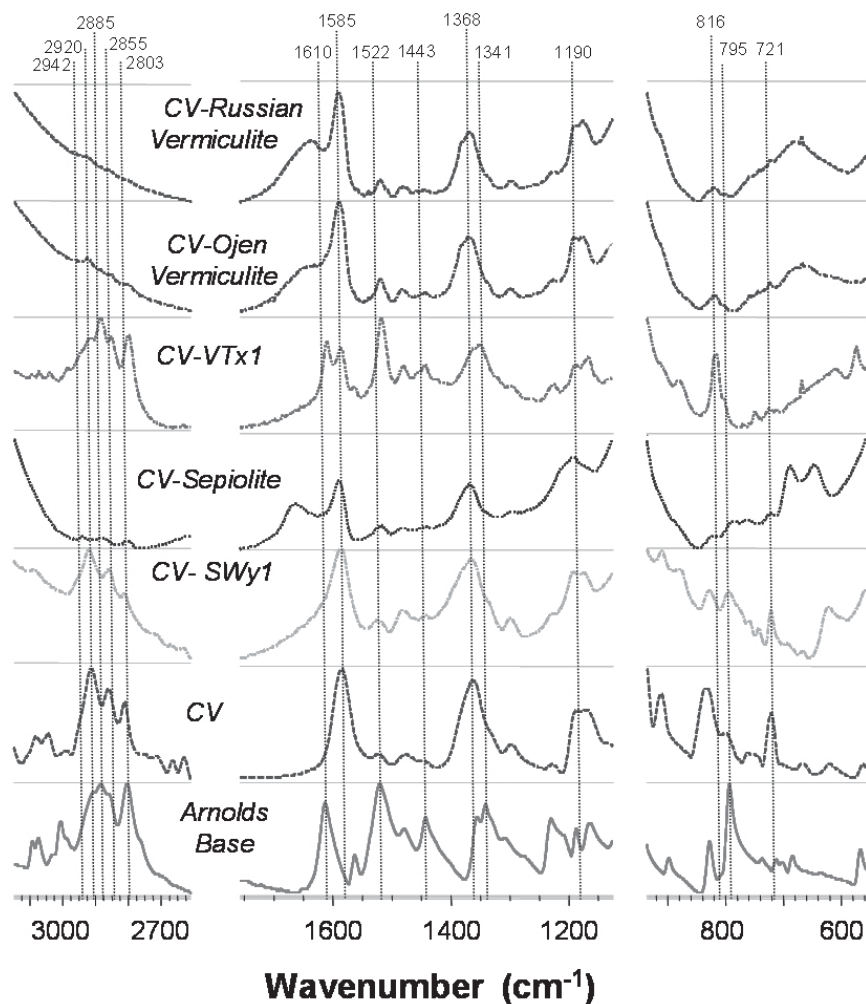


Figure 3. FTIR spectra of CV added to several clays up to 100% of the CEC. CV and Arnolds base spectra are shown for comparison. Three ranges are presented: 550–950, 1100–1700, and 2600–3100  $\text{cm}^{-1}$ .

$\text{CaMg}(\text{CO}_3)_2$ , impurities known to occur in VTx-1 (Suquet *et al.*, 1991). Additional carbonate bending vibrations at 2523 and 2626  $\text{cm}^{-1}$  were also observed.

Assuming that the large differences observed in the CV-VTx-1 sample indicated that the adsorbed dye undergoes a process of decomposition, a series of possible degradation products was measured (results not shown), *e.g.* dimethylaniline (CAS 121-69-7), trimethylaniline (CAS 99-97-8), Michler's ketone (4,4'-Bis(dimethylamino)benzophenone, CAS 90-94-8), Michler's hydrol (4,4'-Bis(dimethylamino) benzhydrol, CAS 119-58-4), and Arnolds base (CAS 101-61-1). Of those, the compound which gave an IR spectrum closest to that of CV-VTx-1, after subtracting the VTx-1 spectrum, was Arnolds base. The hypothesis that CV degrades on VTx-1 to Arnolds base is, therefore, reasonable. Several additional vibrations of the spectra reinforce this conclusion:

(1) The aromatic C–H stretching peaks in the 3050–3100  $\text{cm}^{-1}$  (see Figure 3 and Table 2) region

differ from Arnolds base, which has four bands (3006, 3023, 3073, and 3092  $\text{cm}^{-1}$ ). For CV, only two peaks appeared (3045 and 3081  $\text{cm}^{-1}$ ). Peaks in the spectrum of CV-VTx-1 in that range are similar to those of Arnolds base (Figure 3, Table 2), while CV-SWy-1 had one peak and one shoulder coinciding with the CV spectrum. For all other clays the amounts adsorbed were too small and were masked by the large clay peak at  $\sim 3400$   $\text{cm}^{-1}$ . Baseline corrections in the range 3000–3150  $\text{cm}^{-1}$  showed only two peaks at wavenumbers coinciding with those of CV.

(2) Vibrational modes corresponding to cationic- $\text{N}^+$  vibrations (Brown *et al.*, 1988) were observed between 2400 and 2700  $\text{cm}^{-1}$ , which, though weak, were visible because no other competing peaks were present in this range. The patterns observed for pure CV and CV on OV, RV, SWy-1, and SEP samples were very similar, with two peaks (Table 2), but differed considerably from the CV-VTx-1 sample, which comprised six peaks (Table 2).

Table 2. IR assignments of vibrations on organo-clays with crystal violet (CV) added up to 100% of the CEC. The organo-clay samples are CV on Ojen vermiculite (CV on OV), on Russian vermiculite (CV on RV), on Spanish sepiolite (CV on SEP), on SWy-1 montmorillonite (CV on SWy-1), and on Texas vermiculite (CV-VTx-1).

CV on OV	CV on RV	CV on SEP	CV on SWy-1	CV on VTx-1	Crude VTx-1	pure CV	Arnolds base	Remarks
668 w	668 w	646 d	681 w	668 m	661 m	—	—	Si—O perpendicular <sup>1</sup> mixed Si—O, Al—O <sup>6</sup>
723 w	723	721 w	795 d,m	724 w	—	721 m	794 s	ring C—H para di-substitution <sup>2</sup>
820 m	821 w	816 w	829 d,m	816 s	—	834 s	828 m	
—	—	880 w	881 m	881 m	881 m	—	—	(Mg or Fe)OH deformation <sup>1</sup>
993 s	995 s	981 s	1043 s	994 s	989 s	—	—	Si—O stretching <sup>1,6</sup>
1067 sh	1067 sh	1076 sh	1119 sh	1060 sh	1074 sh	—	—	Si—O stretching (longitudinal) <sup>1,6</sup>
1176	1176	1192 s	1175	1166	—	1170	1165	central C—rings bond <sup>3</sup> ,
1190	1180	—	1191	1189	—	1187	1187	
1368 s	1368 s	1367 s	1365 s	1351 s	—	1362 s	1341 s	symmetric C—H bend,
—	—	—	—	1363 sh	—	—	1355 sh	aromatic-tertiary N stretch <sup>2,4</sup>
—	—	—	—	1443 w	1441 w	—	—	carbonate impurities <sup>6</sup>
—	—	—	—	1443 w	—	—	1442 s	methylene CH <sub>2</sub> scissoring <sup>2,5</sup>
—	—	—	—	1478 m	—	—	1478 m	
1482 w	1480 w	1480 w	1482 m	1481 m	—	1477 m	1478 sh	methyl C—H asymmetric bend <sup>2</sup>
1520 m	1521 w	1518 w	1523 w	1518 s	—	1522 w	1521 s	aromatic ring stretch <sup>2,5</sup>
—	—	—	—	1565 sh	—	—	1563 sh	
1590 s	1590 s	1589 s	1586 s	1610 s	—	1585 s	1613 s	aromatic ring stretch <sup>2,5</sup>
—	—	—	—	1589 s	—	—	—	
1638 b	1636 b	1663 b	—	—	1663 m	—	—	adsorbed/zeolitic water <sup>1,6</sup>
—	—	—	—	2527 w	2523 w	—	—	carbonate impurities <sup>6</sup>
—	—	—	—	2634 sh	2626 sh	—	—	
6 weak bands-2424—	6 weak bands-2425—	6 weak bands-2436—	6 weak bands-2430—	—	—	6 weak bands-2428—	6 weak bands-2426—	cationic-N <sup>+</sup> <sup>5</sup>
2665 w	2666 w	2687 w	2665 w	—	—	2665 w	2663 w	
2799 w	2800 w	2802 w	2812	2797 s	—	2810 s	2802 s	methylamino, N—CH <sub>3</sub> , C—H stretch <sup>2</sup>
—	—	—	—	2850 m	—	—	2859 sh	methylene C—H symmetric stretch <sup>2,5</sup>
2852 w	2851 w	2881 w	2859 s	2884 s	—	2858 s	2884 s	methyl C—H symmetric stretch <sup>2,5</sup>
—	—	—	—	2916 s	—	—	2904 s	methylene C—H asymmetric stretch <sup>2,5</sup>
2921 w	2921 w	2935 w	2920 s	2942 sh	—	2913 s	2960 sh	methyl C—H asymmetric stretch <sup>2,5</sup>
—	—	—	3045 sh	3010 sh	—	3045 sh	3006 s	aromatic =C—H stretching <sup>2,5</sup>
—	—	—	3086 m	3039 m	—	3081 m	3028 sh	
—	—	—	—	3073 d	—	—	3073 d	
—	—	—	—	3092 d	—	—	3092 d	
3414 b	3394 b	3567 s	3621 s	3689 s	3689 s,b	—	—	clay structural O—H stretching <sup>1</sup>

Crystal violet (pure CV), Arnolds base, and crude VTx-1 spectra are shown for comparison. Assignments based on <sup>1</sup>Madejova and Komadel (2001), <sup>2</sup>Coates (2000), <sup>3</sup>Margulies and Rozen (1986), <sup>4</sup>Yariv and Lurie (1971), <sup>5</sup>Brown *et al.* (1988) and <sup>6</sup>Schosseler and Gehring (1996).

b: broad; d: doublet; m, medium; s: strong; sh: shoulder; w: weak.

(3) In the range 2800–2950 cm<sup>-1</sup>, C-H stretching of methyl (—CH<sub>3</sub>) and methylene groups (—CH<sub>2</sub>—) may be indicated (Coates, 2000). The peaks were relatively strong and, when the amounts adsorbed were large, were easily identified (Figure 3). Those peaks also appeared in the pure CV and in the OV, RV, SEP, and SWy-1 clays; only three peaks were observed in VTx-1 clay, and these were attributed to carbonate impurities. The pattern ascribed to cationic-N<sup>+</sup> vibration was absent from the CV-VTx-1 sample.

(4) While the three-aryl-methine dyes have no CH<sub>2</sub> groups (Figure 4), the central carbon atom of the Arnolds base molecule is bound to two hydrogen atoms. The presence of such methylene (—CH<sub>2</sub>—) groups might be observed by the scissoring CH<sub>2</sub> vibrations at 1442 and 1478 cm<sup>-1</sup> notable in the Arnolds base and CV-VTx-1 samples. This assignment is inconclusive as carbonate impurities contribute to the vibration at 1442 cm<sup>-1</sup> for both VTx-1 samples (with and without CV, Table 2). A more conclusive observation for a methylene group can be

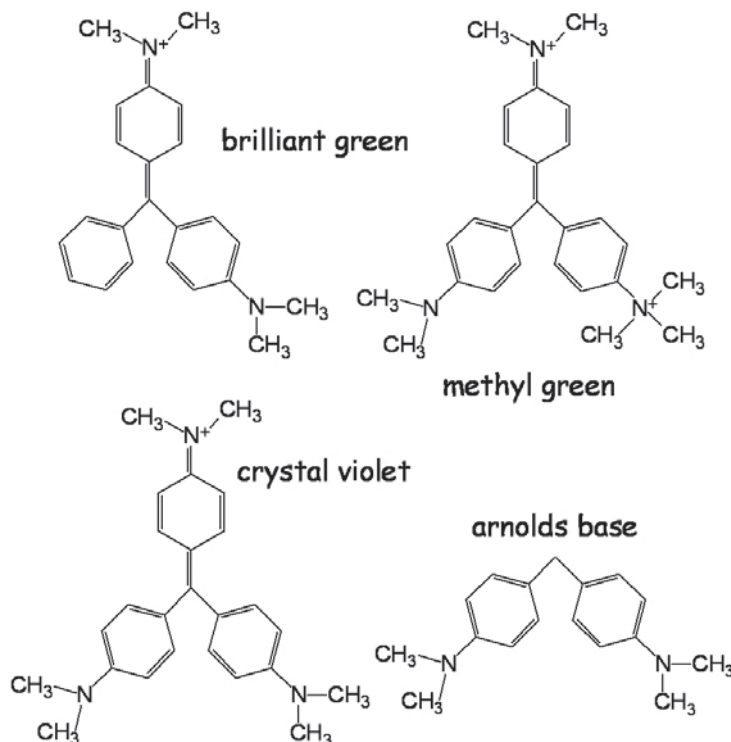


Figure 4. Chemical structure of the triarylmethine dyes: crystal violet (CV), methyl green (MG), and brilliant green (BG), and the degradation product, Arnolds base.

seen in the range  $2800\text{--}2950\text{ cm}^{-1}$ , where possible C-H stretching of methyl and methylene groups are indicated (Coates, 2000); as noted above, these peaks are relatively strong and when the amounts adsorbed are large can be detected easily (Figure 3). For crude CV and for CV on OV, RV, SEP, and SWy-1 clays, only three peaks were observed; for CV-VTx-1, five clear peaks were present, coinciding with similar peaks and shoulders in the Arnolds base spectrum. Closer inspection of those peaks (based on Coates, 2000; Brown *et al.*, 1988) led to the conclusion that the peak at  $2800\text{ cm}^{-1}$  was due to C-H stretching of the methylamino group (N-CH<sub>3</sub>), and appeared in all samples (except, of course, crude VTx-1). Peaks ascribed to the methylene (–CH<sub>2</sub>–) groups appeared, however, only in the Arnolds base and in the CV-VTx-1 sample.

(5) The most prominent pattern that differentiates between IR spectra of Arnolds base and CV-VTx-1 on one hand, and all other organo-clay samples and pure CV on the other hand, is that of ring-stretching vibrations which generally appear as two bands in the  $1500\text{--}1625\text{ cm}^{-1}$  region (Brown *et al.*, 1988). The first group (Arnolds base on CV-VTx-1) exhibited (Figure 3) a very strong peak at  $\sim 1520\text{ cm}^{-1}$ ; the equivalent peak for all other samples at the same wavenumber was very weak. The second peak ascribed to the same vibration is observed at  $1610\text{ cm}^{-1}$  in the Arnolds base spectrum, but at  $1585\text{ cm}^{-1}$  for CV on the OV, RV, SEP, and SWy-1 clays. The CV on VTx-1 spectrum exhibited both vibrations ( $1585\text{ cm}^{-1}$ , corre-

sponding to CV; and  $1610\text{ cm}^{-1}$ , related to Arnolds base) indicating that not all of the CV was degraded, whereas crude VTx-1 showed no peak at all in this region. For smaller concentrations of CV added to VTx-1 (results not shown), the peak at  $1585\text{ cm}^{-1}$  decreased considerably, in comparison with the vibration at  $1610\text{ cm}^{-1}$ , indicating less CV and more Arnolds base.

All the FTIR data indicate that degradation of CV appears to be a feature of VTx-1 only. However, at large CV concentrations (results not shown), equivalent to 300% of the CEC (*i.e.*  $0.42\text{ mol}_e/\text{kg}$ ), some degradation may be observed for SEP also. This point requires further study.

Decomposition of dyes in minerals with large charge densities have been reported previously. The rate and/or extent of decomposition of cyanine dyes was controlled by the surface-charge density of the layered silicate tested (Budjak *et al.*, 2002a, 2002b). Aggregates of dye cations were stable at surfaces with low and intermediate charge densities, while dye molecules decomposed on surfaces of minerals with high charge densities.

#### Visible spectroscopy of CV clays

Interactions between clay minerals and organic dyes cause changes in the chemical properties of the chromophores, yielding changes in the visible-range spectrum. Such changes are ascribed to the formation of molecular aggregates of the dye cations (Budjak, 2006). Free CV in solution exhibited a peak at  $588\text{ nm}$  with a

shoulder at 544 nm (Figure 5). Bujdak and Iyi (2002) studied dye aggregation of CV and other triarylmethine dyes using visible spectroscopy. The absorption bands at 544 nm were assigned by Bujdak and Iyi (2002) to CV-adsorbed dimers. Face-to-face association between dye-adsorbed molecules (H aggregates) exhibited hypsochromic shifts, yielding absorption at 480–520 nm. Less densely packed, face–tail CV aggregates (J-aggregates), absorb light at greater wavelengths (600–620 nm, bathochromic shift) suggesting that adsorption of CV to SWy-1 montmorillonite (Figure 5) causes the formation of dimers (peak at 544 nm), whereas H and J aggregates might be observed as shoulders at 498 and 610 nm, respectively. Large amounts of dimers and aggregates coincide with large CV-CV interactions on the surface of montmorillonite, as reported by previous studies (*e.g.* Rytwo *et al.*, 1995). Slightly different effects are observed for CV adsorbed on SEP (Figure 5). Here, the monomer peak at 588 nm remains the principal vibration and a slight increase at 544 nm indicates the notable presence of dimers. The shoulder indicating J-aggregates is larger than that due to H aggregates. Such results coincide with previous studies (Bujdak and Iyi, 2002) where relatively higher charge-density surfaces (as in montmorillonite) induced the formation of H-aggregates, but smaller layer charges (as in SEP) were reflected in the reduction of the H-aggregation in favor of monomers, and less densely packed J-aggregates. However, the spectrum of CV adsorbed on high layer-charge vermiculite is almost identical to that of free CV in solution, indicating almost no dye-dye interaction, with almost no change after 10 min. The formation of pseudo-iso-cyanine (PIC) dye aggregates while adsorb-

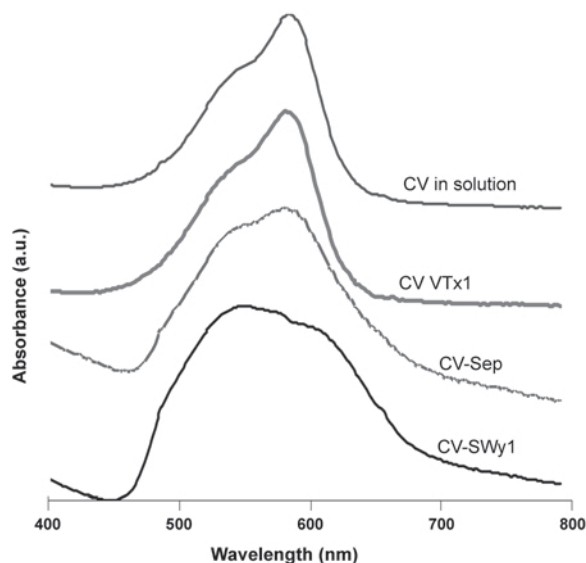


Figure 5. Visible spectra of free CV in solution, CV adsorbed to SWy-1 (CV-SWy1), SEP (CV-Sep), and VTx-1 (CV-VTx-1). All spectra are shown in arbitrary absorption units, normalized to the largest peak.

ing on montmorillonite was suppressed by the presence of ethylene glycol in solution (Miyamoto *et al.*, 1999), and was explained by those authors as the effect of the stronger affinity of PIC for ethylene glycol, which could alter the adsorption state of the dye molecules on clay surfaces and, consequently, the state of aggregation. However, the lack of aggregation in VTx-1 is a function of the slow kinetics of adsorption, combined with the degradation observed in FTIR measurements. Molecules are attracted at a slow rate to the surface and decomposed to smaller products due to the structural tension caused by the high charge (Bujdak *et al.*, 2002a, 2002b). Because at any given time only a small number of CV molecules was bound to the surface, and scarcely dispersed, no dimers or aggregates were formed, and no influence on the chromophoric unit was observed.

#### FTIR spectra of adsorbed BG and MG

In order to check whether such degradation is specific to CV or occurs in other similar dyes, similar experiments were performed with brilliant green (BG) and methyl green (MG) (see Figure 4 for the chemical structures). The FTIR spectra of both dyes, bound to SWy-1 montmorillonite, were very similar to those of the free dyes (Figure 6). The small differences between the MG and MG-SWy-1 spectra are due to the fact that MG adsorbs to smectite as carbinol (Rytwo *et al.*, 2000). However, more significant changes for both dyes occurred when adsorbed onto VTx-1. The most noticeable change was the ring C–H vibrations at  $\sim 1520\text{ cm}^{-1}$  present in the MG- and BG-VTx-1 spectra, but absent from all other spectra. Similar results were observed for CV-VTx-1, indicating degradation of the dye, and possible formation of Arnolds base (Figure 3, Table 2). Additional changes in the ring doublet at  $1580\text{--}1610\text{ cm}^{-1}$  reinforce this hypothesis. Similar results were observed in other regions of the FTIR spectra (results not shown).

## CONCLUSIONS

Adsorption of CV was tested on three vermiculites. While concentrations of CV in solution when added to OV and RV clays remained unchanged, indicating no adsorption or degradation of the dye, CV concentrations in solution with VTx-1 were depleted and eventually no dye remained in the solution. No increase in the basal spacing of the clay platelets was observed even though the amounts removed from the solution were  $>3$  mole dye  $\text{kg}^{-1}$  clay ( $\sim 150\%$  of the CEC of the clay).

Visible-spectrum measurements of CV adsorbed on VTx-1 showed no aggregation between the dye and adsorbed molecules, and no influence on the chromophoric units. Such behavior differs considerably from that observed for CV-SWy-1 and CV-SEP.

FTIR measurements indicated that CV was not only adsorbed on the clay, but also partly decomposed to

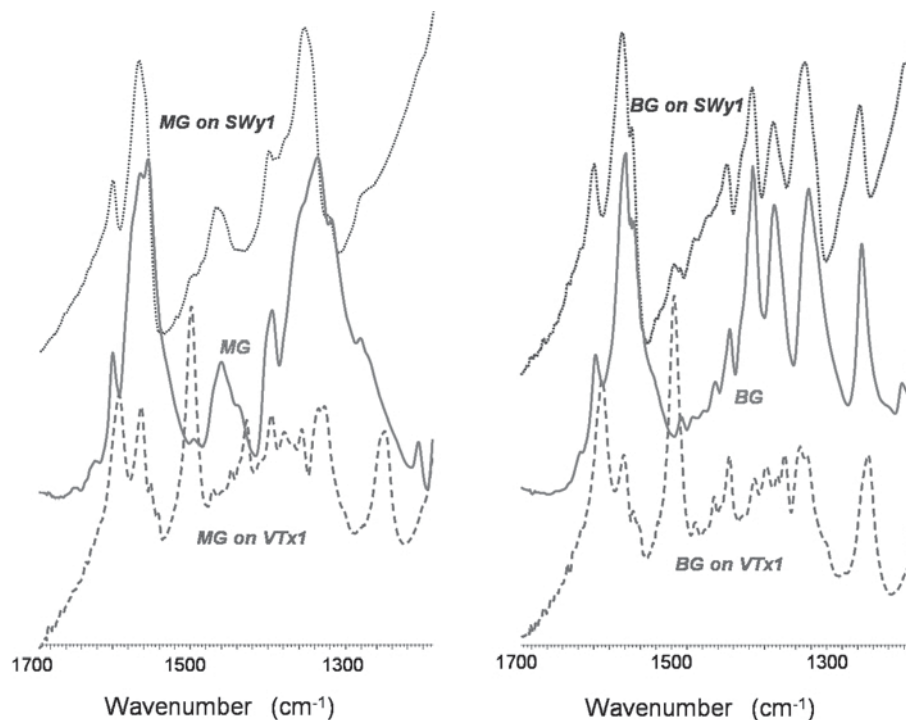


Figure 6. FTIR spectra in the 1200–1700  $\text{cm}^{-1}$  range of free brilliant green (BG), BG adsorbed on VTx-1, BG adsorbed on SWy-1, free methyl green (MG), MG adsorbed on VTx-1, and MG adsorbed on SWy-1.

other compounds, while CHNSO measurements indicated that all of the organic carbon adsorbed remained attached to the surfaces of the clay platelets. While the exact identity of the degradation products requires additional study, the similarity of the FTIR spectra suggests that Arnolds base is one of the products. Similar degradation was observed for two other triarylmethine dyes (BG and MG). In all cases, decomposition was observed only on VTx-1 clay. The hypothesis proposed here, based on that of Bujdak *et al.* (2002a, 2002b), is that due to the relatively large size of the three-arylmethine dyes compared with the size of the charged site on vermiculite, structural tension leads to a significant destabilization of the molecule and decomposition at its molecular center (the central carbon between the three aryl groups, Figure 5). Since most charges on VTx-1 clay are due to tetrahedral substitutions (Jaynes and Bigham, 1987), close and strong inner-sphere complexes may play a crucial role in such degradation (H. Stanjek, 2008, personal communication). Products of the decomposition of CV absorb UV but not visible light, so they cannot be observed in the visible spectrum but are seen clearly in FTIR measurements.

Additional experiments are planned in order to elucidate: the exact path of the process; the identity of the degradation products; and the influence of the composition of VTx-1 clay (by testing different exchangeable cations and the reactivity of the impurities), in order to try to explain the different behaviors observed for various vermiculites.

The kinetics of degradation of the dye indicate that when VTx-1 vermiculite was not sonicated an ~11-day delay occurred before initiation of the process. When sonication of the clay suspension was performed, the process began immediately. Ignoring the delay, the kinetic parameters for the removal of the dye from solution ( $k$  and  $q_e$ ) were similar.

The results presented here could lead to environmental applications, such as the use of sonicated Texas vermiculite as an effective catalytic agent for the degradation of triarylmethine dyes from textile or other industrial effluents. The benefit of such processes is that no oxidation, heating, or photoactivation would be needed.

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