Journal of Thermal Analysis and Calorimetry, Vol. 84 (2006) 1, 225–231

ADSORPTION OF FAST GREEN AND ERYTHROSIN-B TO MONTMORILLONITE MODIFIED WITH CRYSTAL VIOLET

G. Rytwo[1,2*], *R. Huterer-Harari*[1], *S. Dultz*[3] *and Y. Gonen*[1]

[1]Tel Hai Academic College, Biotechnology and Environmental Sciences Department, Upper Galilee 12210, Israel
[2]MIGAL, Galilee Technological Center, Kiryat Shmona, Israel
[3]Institute of Soil Science, University of Hannover, Herrenhäuser Str. 2, 30419 Hannover, Germany

Adsorption of erythrosin-B (EB) and fast green (FG) to a non-charged organosmectite based on crystal violet adsorbed up to 100% of the cation exchange capacity (CEC) was tested. Adsorption isotherms of EB and FG were prepared at 3, 24 and 50°C. All isotherms are of H-type reaching loads of approximately up to 20% of the original CEC of the crude montmorillonite (up to 0.15 and 0.10 mol dye kg^{-1} clay for EB and FG, respectively). Adsorption decreases with temperature, indicating an exothermic process. Enthalpy was evaluated using van't Hoff equation, yielding approximately –20 kJ mol^{-1} for both dyes.

Keywords: *adsorption, crystal violet, erythrosin-B, fast green, isosteric enthalpy of adsorption, montmorillonite, organoclay*

Introduction

Adsorption of dyes to smectitic clays was widely studied and extensively reviewed [1–3]. In this study we tested the adsorption of two anionic dyes, erythrosin-B (EB) and fast green (FG), to an organoclay prepared by pre-adsorbing crystal violet (CV) to Wyoming montmorillonite (SWy-1) up to 100% of the cation exchange capacity (CEC). Fast green FCF and Erythrosin-B are anionic dyes, highly soluble in water, and widely used in biology [4, 5]. CV is a cationic tri-arylmethane dye, used industrially in inks and dyes. Sorptive properties of smectite to organic molecules can be modified by exchanging the inorganic and hydrated exchangeable cations with large organic cations. The presence of organic cations creates a hydrophobic surface, efficient for sorption of large organic compounds [6]. Investigators differentiate between 'organophilic' and 'adsorptive clays': the first term is used for large quaternary ammonium cations, whereas the latter- for smaller ions [3]. The covering changes the surface and interfacial properties of the sorbent. The organoclay then takes on the surface properties of the organic moiety that is at or near the new surface [7].

The organoclay used in this study was prepared by exchanging the inorganic cations with CV. Previous studies show that all the inorganic cations of the crude montmorillonite are exchanged when the CV adsorption is at 100% of the cation exchange capacity (CEC) [8].

Borisover *et al.* (2001) [9] define organo clays, based on an organic- cationic dye as adsorptive organoclays, and assume that by using such organic molecules it will be possible to combine the effectiveness of the adsorptive mechanism with a more capacious organic layer as in organophilic clays.

Organoclays based on montmorillonite and CV were widely studied for analytical purposes or practical applications [9–12]. IR measurements show that when CV was adsorbed up to the CEC of the clay, the organoclay complex has no hygroscopic water in it [13], and the nanoparticles interact strongly with other organic molecules.

The goal of this study is to test the adsorption of two large organic molecules to a CV-montmorillonite organoclay, aiming the development of nanomaterials with high sorptive properties, which might be applied in industrial and environmental applications.

Materials and methods

Wyoming montmorillonite was purchased from the Source Clays Repository of The Clay Minerals Society (Columbia, MO). Detailed specification of the clay parameters can be found in Rytwo and Tropp (2001) [14]. CV was obtained from Fluka Chemica (Fluka Chemie AG, Buchs, Switzerland). EB and FG were purchased from Spectrum Inc. (Gardena, Ca). All materials were used without further treatment or purification.

An organoclay with CV up to 100% of the CEC was prepared by adding 1 g dry clay to 200 mL of distilled water, and stirring it for several minutes. When the suspension was homogenous CV powder was added, and stirring continued for two hours. For the particle charge density (PCD) and thermal analysis measure-

---

* Author for correspondence: rytwo@telhai.ac.il

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

ments small amounts of organoclays containing CV at several ratios of the CEC were prepared following the same guidelines. The suspensions were filtered, and the powder was dried and used for the measurements. Amount of CV adsorbed in all cases was calculated by sampling and filtering the suspension, and measuring the remaining dye by UV-Visible spectroscopy using an HP 8452A spectrophotometer, at 588 nm for CV.

Adsorption experiments of EB and FG to the CV-clay suspensions were performed at three different temperatures: an industrial refrigerator (3±1°C), room temperature (24±1°C), and a laboratory incubator (50±0.5°C). For each dye (EB or FG) stock 1 mM solutions were prepared. To 1 mL of the organoclay suspension the desired amount of dye was added, and the volume was completed to 30 mL with distilled water. The final clay concentration in suspension was 0.15 g L^{-1}. Experiments were performed in triplicate, and all solutions, distilled water and bottles were brought to equilibrium at the desired temperature, before preparing the samples. All samples were stirred manually at their equilibrium place (refrigerator, room or oven) 4 times per day.

After 3 days suspensions were filtered using a 0.47 μm Whattman filter, and concentrations of the dyes were calculated after measuring optical density by UV-Visible spectroscopy using an HP 8452A spectrophotometer, at 526 nm for EB, and 624 nm for FG. No adsorption of the anions was measured on the filters. CV remaining in solution is very low, since almost all of it was adsorbed, however a mathematical elaboration of the spectra was performed in order to cancel the influences of the remaining CV, by a spectra-subtraction computer program prepared using MATLAB (Gonen, 2003, unpublished results). Competitive adsorption experiments were prepared following the same procedure.

The surface charge density of the organoclay CV clays with different loads was measured by a titration with polyelectrolytes [15, 16] using a particle charge detector (MÜTEK; PCD 03). For the determination of the microstructure an environmental scanning electron microscope (Fei, Quanta 200) was used. Back scattered electron images were taken at room temperature and at high vacuum. The thermogravimetric (TG) and the differential thermal analysis (DTA) measurements were carried out simultaneously with a Netzsch STA 429 instrument. The heating rate was 5°C min^{-1}.

Results and discussion

Electrokinetic effects are widely used to characterize the charge distribution around aqueous colloid particles [15]. In Table 1, crude montmorillonite shows a high negative value (–138 $mmol_c$ kg^{-1}), as is expected, considering isomorphic exchanges at the clay lattice that lead to negative charges compensated with inorganic exchangeable cations [6]. Adsorption of CV at loads lower than the CEC changes the surface properties causing decrease in the electrokinetic surface potential, but the value measured is still negative. Adsorbed amounts of 100% of the CEC, neutralize completely the negative charge, and particles became slightly positive. Similar values (close to zero) were measured using the same technique, for the adsorption of mepiquat and difenzoquat on montmorillonite up to the CEC [16]. Whereas in those previous studies no charge reversal was observed, increase in the amount of CV leads to very high positive charge, almost 100% of the initial charge (with opposite sign). These results indicate that at high loads of CV the adsorption of additional cations to a positively charged surface can not be ascribed to coulombic interactions, and arise from hydrophobic interactions between the organic adsorbed moieties.

Table 1 Electrokinetic surface charges for CV-organoclays, as measured using a particle charge detector. The load of CV appears as percentage of the CEC of the clay

Sample	Electrokinetic surface charge/ average	sd. dev.
	$mmol_c$ kg^{-1}	
Crude smectite	–137.9	2.9
CV 60% CEC	–16.2	3.8
CV 100% CEC	7.0	0.4
CV 150% CEC	82.3	1.3
CV 200% CEC	127.1	0.3

The lack of hygroscopic water in the organoclay based on CV up to 100% CEC is confirmed by thermal analysis. Figure 1 shows TG and DTA analysis of CV-montmorillonite complexes, with added amounts of up to 400% CEC. For loads of up to 120% CEC almost all the added CV adsorbed to the clay, as observed in previous studies [8, 13]. At no CV adsorbed, an endothermic peak is observed at 105°C indicating dehydration. This peak decreases gradually, and disappears at 80% of the CEC. Those results are confirmed with TG measurements, that show loss of mass up to 100% CEC, and almost no additional loss at higher adsorbed amounts, up to 200°C. Further losses of mass are found at about 600°C in all samples, and are ascribed to the dehydroxylation of the montmorillonite [17]. TG plot shows that the thermal decomposition of the adsorbed CV starts at about 250°C. These findings coincide with thermo-XRD recent studies [18], where several adsorbed dyes oxidize forming charcoal at similar temperatures. DTA plot shows in the course of the thermal decomposition of the CV,

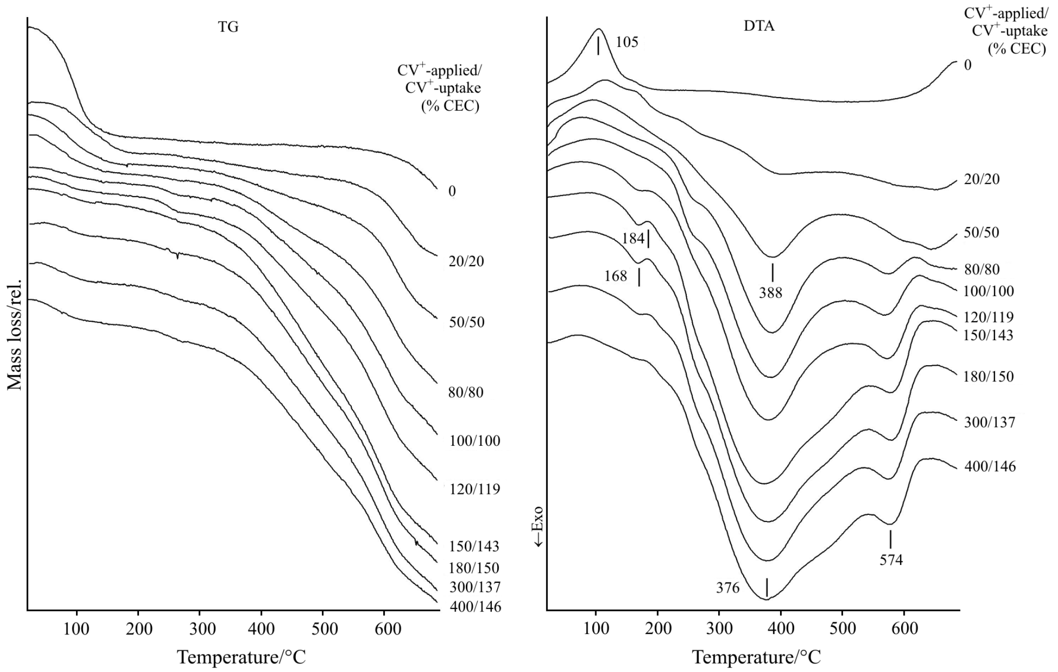

Fig. 1 TG and DTA plots for SWy-1 with CV added between 20–400% of the CEC. Amounts added and adsorbed as a function of the CEC appear at the figure

two main exothermic reactions with maxima at 380 and 570°C. A reaction at about 180°C is found with increasing levels of CV saturation. It is difficult to determine due to the shape of the line, but it seems as a slightly exothermic process. Previous studies [10, 19], ascribed a similar exothermic peak at 215°C to the formation of 'organic water'. Such peak has not been detected in CV not bound to clay.

Figure 2 shows adsorption isotherms of both dyes to the organoclay based on CV adsorbed up to 100% CEC. It can be seen that EB (Fig. 2a) adsorbs completely at all temperatures up to added amounts of 0.08 mol kg^{-1}. Complete adsorption reaches higher values at low temperature (0.10 mol kg^{-1} at 3°C). Adsorption decreases with temperature, implying an exothermic process [20]. In the case of FG (Fig. 2b), complete adsorption is up to added amounts of 0.05 and 0.07 mol kg^{-1} for high and low temperature, respectively. As in the case of EB, decrease with temperature is observed, but amounts adsorbed are lower than those measured for the other dye. Lower adsorption is ascribed to the fact that FG molecules are considerably larger than EB molecules, leading to steric effects that limit the maximum amount of FG that might be accommodated upon the sorbent. It should be emphasized that adsorption of both dyes to crude

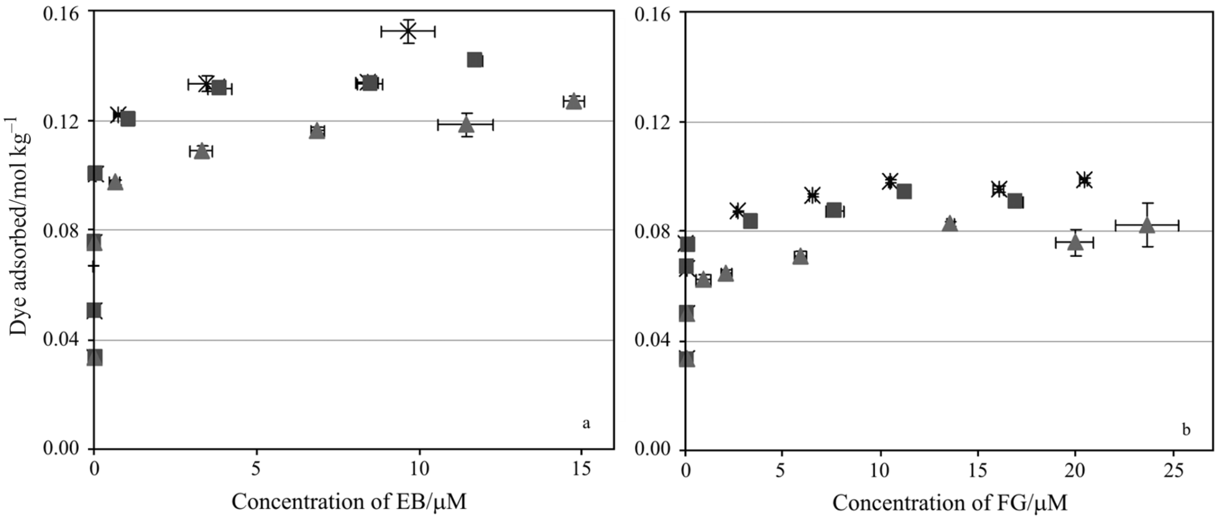

Fig. 2 Adsorption isotherms of a – EB and b – FG to CV-clay, at 3°C (asterisks), 24°C (rectangles) and 50°C (triangles)

montmorillonite is less than 0.02 mol kg^{-1} in all cases tested (Gonen and Ganigar, 2005, unpublished results). Thus, the modification of the clay surfaces making it an organophilic clay, makes it suitable to adsorb those dyes at large amounts. Even though the possibility of electrostatic interaction between the slightly positive organoclay (Table 1) and the anionic dyes cannot be rejected, the relatively large amounts adsorbed insinuate that organophilic interactions play an important role in the adsorption.

When considering the amounts of dye adsorbed, and transforming it to mass, it should be noted that the organoclay particles with anionic dye adsorbed contain per gram of clay mineral 0.8 mmol CV$^+$ (M.W. of the cation: 372 g mol^{-1}), and about 0.1 mmol EB or FG (app. 800 g mol^{-1}). Thus, it contains 0.38 g organic compounds, meaning 27% of the total mass. In addition to that, the mass of anionic dye adsorbed per gram of organocation in the organo clays, may reach 0.4 g EB g^{-1} CV, as calculated for an adsorption of 0.14 mol kg^{-1}. Accommodation of such large amount of organic molecules, needs a large open surface area. Figure 3 shows an environmental scanning electron microscope (ESEM) photograph at a 25 kV voltage (×8000 magnification) of the crude SWy-1 clay (Fig. 3a), and the organoclay used in this study (Fig. 3b). As the surface of the crude clay seems planar and smooth at this magnification, adsorption of CV up to the CEC, increases the porosity, giving the compound a sponge-like texture. Large amounts of organic molecules might sorb to the increased surface area exposed.

All the adsorption isotherms presented in Fig. 2, are of H-type, indicating high affinity between the sorbent and the adsorptive [21]. Langmuir equation is usually used for L-type isotherms, but it might be applied for H-type by avoiding the points with complete adsorption. The basic assumptions of the Langmuir equation are [20] (a): adsorption cannot proceed beyond monolayer coverage, (b): all sites are equivalent and surface is uniform, (c): the ability of molecules to adsorb is independent of the occupation of neighboring sites. Although most assumptions are not valid for heterogeneous surfaces, Langmuir isotherm is widely used for qualitative and descriptive processes in soil and clay minerals [21], and can be expressed as:

$$q = \frac{K_L S_{\max} C}{(1 + K_L C)} \quad (1)$$

where q is the amount adsorbed (mol kg^{-1}), C is the equilibrium concentration of the adsorptive (mol L^{-1}), $S_{\max}$ is the maximum amount of adsorptive that can be adsorbed at monolayer coverage (mol kg^{-1}), and K_L, is a coefficient related to the binding strength of the adsorptive to the sorbent, at the specific experimental conditions (L mol^{-1}). Since the amount adsorbed (q) and the equilibrium concentration (C) were measured, we may evaluate $S_{\max}$, and the Langmuir coefficient (K_L) for each temperature.

$S_{\max}$, was evaluated from all isotherms of each dye, assuming it is not affected by the temperature, since it represents the relationship between the area of the sorbent, and the contact area of the adsorptive. The values of $S_{\max}$ were deduced from Fig. 2 as 0.14 and 0.10 mol kg^{-1} for EB and FG, resepectively. The lower value for FG is ascribed to the larger size of the molecule: the triarylmethane skeleton of FG is bounded to two additional aromatic rings connected to SO_3 groups. EB structure is based on a relatively smaller xanthene skeleton. K_L values were calculated for each isotherm,

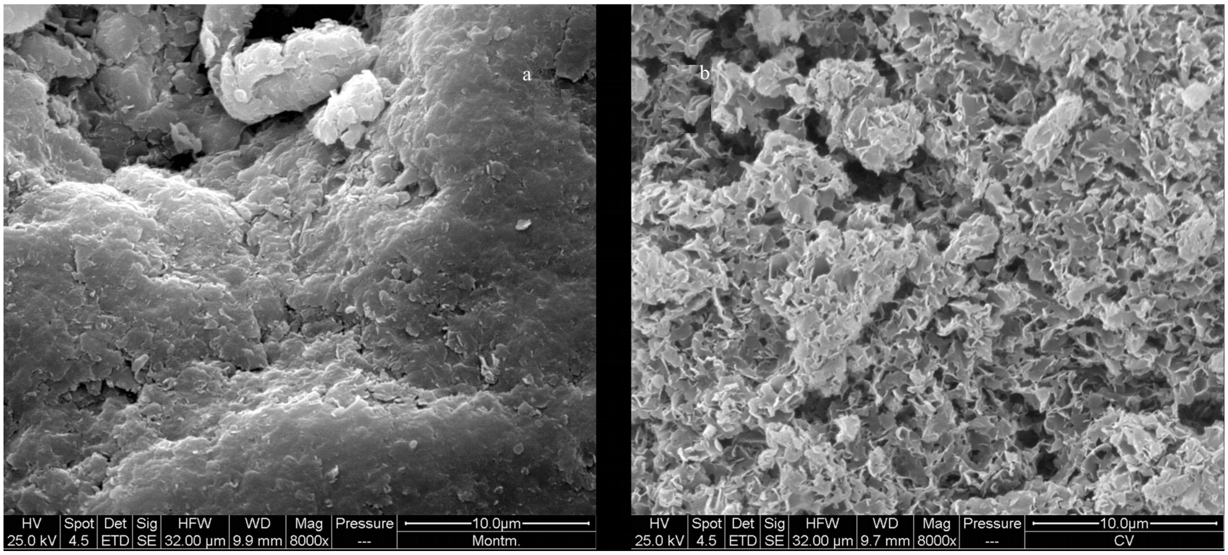

Fig. 3 ESEM backscattered images of the microstructure of a – the original SWy-1 crude montmorillonite and b – montmorillonite with CV adsorbed up to 100% CEC. Both images are at ×8000 magnification

Table 2 Langmuir coefficient (K_L) and maximum amount of dye that can be adsorbed as monolayer (S_{max}), for the adsorption of EB and FG on CV-clay

Dye	T/°C	K_L/L mol^{-1}	S_{max}/ mol kg^{-1}	R^2
EB	3	$9.32\cdot10^6$	0.14	0.897
EB	24	$5.62\cdot10^6$	0.14	0.907
EB	50	$3.15\cdot10^6$	0.14	0.936
FG	3	$2.51\cdot10^6$	0.10	0.916
FG	24	$1.32\cdot10^6$	0.10	0.787
FG	50	$0.72\cdot10^6$	0.10	0.919

and are concentrated in Table 2. Determination coefficients (R^2) were evaluated by comparing the measured adsorbed amounts (Fig. 1) with those calculated by Eq. (1) using the parameters presented at Table 2.

K_L for both dyes decreases with temperature, implying exothermic reactions [20]. Such assumption is reinforced below; with calculations using van't Hoff equations. Both K_L and S_{max} are larger for EB at all temperatures, as expected, considering the adsorbed amounts shown in Fig. 2.

The larger binding affinity of EB is confirmed in competition experiments (Table 3): when adding identical amounts of dye to the organo clay, EB adsorbed amounts remained unaffected by the presence of FG, and adsorbed amounts were almost the same than those at Fig. 2, with complete adsorption when added amounts are up to 0.10 mol kg^{-1}. On the other hand, adsorption of FG is strongly influenced by competition, and total adsorption at low temperature is below 0.05 mol kg^{-1}. The differences between the dyes increase at higher temperatures (50°C): total adsorption of FG reaches 0.032 mol kg^{-1}, about 60% of the total adsorption measured without competition at the same temperature (Fig. 2b).

The variations of K_L values with temperature (Table 2) can be used to determine $\Delta_{ad}H^ø$, the isosteric enthalpy of adsorption [20], which is the standard enthalpy of adsorption at a fixed surface coverage. Since K_L is essentially an equilibrium constant, van't Hoff equation might be used:

$$\left(\frac{\partial \ln K_L}{\partial T}\right)_P = \frac{\Delta_{ad}H^ø}{T^2R} \tag{2}$$

in which R represents the gas constant (R=8.314 J mol^{-1} K^{-1}). Adapting Eq. (2) to a more convenient way, yields:

$$\left(\frac{\partial \ln K_L}{\partial 1/T}\right)_P = -\frac{\Delta_{ad}H^ø}{R} \tag{3}$$

Then, by plotting ln(K_L) as a function of 1/T, a linear relationship is obtained, in which $\Delta_{ad}H^ø$ can be directly deduced by the slopes of the lines. Figure 4 shows such plots presenting a very good fit between the linear line and the ln of the Langmuir coefficients for both dyes (R^2>0.98). Such linearity indicates that $\Delta_{ad}H^ø$ almost does not change with temperature, within the range the experiments were performed (3–50°C). The slopes in Fig. 4 imply $\Delta_{ad}H^ø{}_{EB}$= –17.1 kJ mol^{-1}, $\Delta_{ad}H^ø{}_{FG}$= –19.7 kJ mol^{-1}. As it can be seen adsorption of both anionic dyes to CV-clay is exothermic, and with relatively similar change of enthalpy. Enthalpies of adsorption of organic molecules to clay minerals are generally exothermic [20], since molecules leaving the solution and

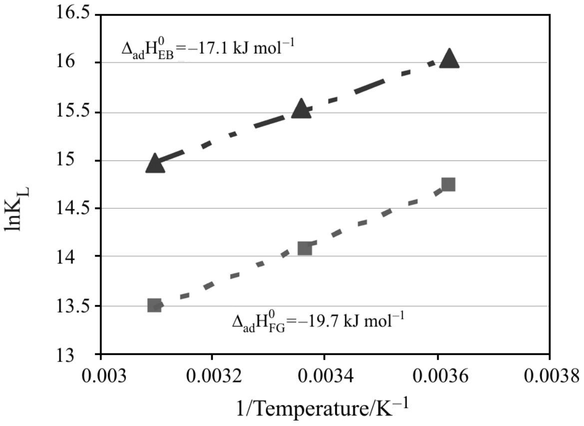

Fig. 4 Logarithm of K_L as a function of the reciprocal of the absolute temperature. EB and FG values are indicated using triangles and squares, respectively. Lines are calculated by linear regression for each dye, and in both cases R^2>0.98. Isosteric enthalpies of adsorption ($\Delta_{ad}H^ø$) are evaluated from the slopes, using Eq. (3)

Table 3 Adsorbed amounts of EB and FG in competitive adsorption experiments, as a function of the amount of dye added, at 3 and 50°C

Total dye added/ mol kg^{-1}	T/°C	FG		EB	
		added/mol kg^{-1}	adsorbed/mol kg^{-1}	added/mol kg^{-1}	adsorbed/mol kg^{-1}
0.100	3	0.050	0.046±0.2%	0.050	0.05±0.1%
0.150	3	0.075	0.045±1.1%	0.075	0.074±0.2%
0.204	3	0.102	0.047±6.3%	0.102	0.092±2.2%
0.100	50	0.050	0.033±3.0%	0.050	0.050±0.0%
0.150	50	0.075	0.029±4.5%	0.075	0.073±0.3%
0.204	50	0.102	0.032±0.3%	0.102	0.092±1.1%

becoming attached to the surface, lead to a decrease in the dispersion of the energy – meaning a decrease in the entropy [22]. Processes with decreasing entropy might be spontaneous only if they are exothermic. However sorption processes in crude clays are usually exchange processes, and the release of inorganic cations and hydration shells might cause an overall increase in entropy [23], and endothermic adsorption processes were indeed reported [23–25] in several cases.

In this specific study, the adsorption is not accompanied by exchange or release of ions. Neither release of water molecules is expected, since CV-clay at this load has almost no hygroscopic water, as was measured by infrared measurements [13], and confirmed in our thermal analysis measurements. Thus, no increase in entropy is observed, and since the adsorption of the dyes to CV-clay is spontaneous and occur, exothermic processes were expected, as they were indeed evaluated by means of the van't Hoff equation.

Conclusions

An organo-clay with CV up to 100% of the CEC was prepared, leading to almost neutral sorbent. Particle charge density of the compound demonstrated that the remaining charge was about 5% only of the initial montmorillonite charge density, and with an opposite sign, indicating slightly positively charged particles. TG and DTA demonstrate complete dehydration at the loads used for this adsorption study. Adsorption isotherms of EB and FG to such organoclay at three different temperatures: 3, 24 and 50°C are of H-type indicating high affinity between sorbent and adsorptive, reaching loads up to 0.15 and 0.10 mmol dye g^{-1} clay mineral for EB and FG, respectively. We assume that such high affinity might be induced by interaction between phenyl rings [26]. Lee *et al.* (2001) [27] studied adsorption of two dyes to CV clay and received considerably lower values. We ascribe the difference between our results, to the fact they performed the experiments at pH=3. In their study they also show that adsorption of CV at pH=7 is two folds the adsorption at pH=3.

Adsorption of both dyes decreases with temperature, indicating that the process is exothermic. Isosteric enthalpies of adsorption ($\Delta_{\mathrm{ad}}H^{\o}$) were evaluated by means of the van't Hoff equation, based on the changes in Langmuir adsorption coefficients as calculated from the adsorption isotherms. Calculations yielded enthalpies of –17.1 and –19.7 kJ mol^{-1} for EB and FG, respectively. Competitive adsorption experiments show that adsorption of EB is not influenced by temperature, and it is almost complete up to 0.10 mmol g^{-1}. Adsorption of FG decreases with temperatures, and reaches values considerably lower than those obtained without competition. The relative mass of organic molecules adsorbed to the organoclay is high, implying that such compound might have industrial and environmental applications as sorbent.

Abbreviations

CEC	cation exchange capacity
CV	N-[4-[Bis[4-(dimethylamino)-phenyl]methylene]-2,5-cyclohexadien-1-ylidine]-N-methyl-methanaminium chloride (chrystal violet)
DTA	differential thermal analysis
EB	2',4',5',7'-tetraiodofluorescein disodium salt (erythrosin-B)
FG	N-Ethyl-N-(4-[(4-ethyl[(3-sulfophenyl)methyl] aminophenyl)-(4-hydoxy-2-sulfophenyl)methylene]-2,5-cyclohexadien-1-ylidene)-3-sulfobenzenemethanaminium hydroxide inner salt, disodium salt (fast green)
PCD	particle charge density
TG	thermogravimetric analysis
SWy-1	Wyoming montmorillonite
UV	ultraviolet
$\Delta_{\mathrm{ad}}H^{\o}$	isosteric enthalpy of adsorption

References

1 S. Yariv, Inter. J. Trop. Agric., 6 (1988) 1.

2 S. Yariv, Staining of Clay Minerals and Visible Absorption Spectroscopy of Dye-Clay Complexes, in: Organo-clay Complexes and Interactions. S. Yariv and H. Cross (eds), Marcel Dekker Publ. 2002, pp. 464–566.

3 S. Yariv, Introduction to Organo-Clay Complexes and Interactions, in: Organo-clay Complexes and Interactions. S. Yariv and H. Cross (Eds), Marcel Dekker Publ. 2002, pp. 39–112.

4 Y. F. Li, C. Z. Huang and M. Li, Anal. Sci., 18 (2002) 177.

5 L. J. Thomson, T. Xing, J. L. Hall and L. E. Williams, Plant Physiol., 102 (1993) 553.

6 C. T. Johnston, Sorption of Organic Compounds on Clay Minerals: A Surface Functional Group Approach, in CMS Workshop Lectures, 8, Organic Pollutants in the Environment, Sahwney, B. ed. The Clay Mineral Society, Boulder CO, 1996 pp. 1–44.

7 R. F. Giese and C. J. van Oss, Organophilicity and Hydrophobicity of Organo-Clays, in: Organo-clay Complexes and Interactions. S. Yariv and H. Cross (Eds), Marcel Dekker Publ. 2002, pp. 175–191.

8 G. Rytwo, C. Serban, S. Nir and L. Margulies, Clays Clay Miner., 39 (1991) 551.

9 M. D. Borisover, E. R. Graber, F. Bercovich and Z. Gerstl, Chemosphere, 44 (2001) 1033.

10 I. Lapides, S. Yariv and D. Golodnitsky, J. Therm. Anal. Cal., 67 (2002) 99.

11 S. H. Lee, D. I. Song and Y. W. Jeon, Environ. Technol., 22 (2001) 247.

12 T. Polubesova, S. Nir, Z. Gerstl. M. Borisover and B. Rubin, J. Environ. Qual., 31 (2002) 1657.

13 G. Rytwo, S. Nir and L. Margulies, Soil Sci. Soc. Am. J., 59 (1995) 554.
14 G. Rytwo and D. Tropp, Appl. Clay Sci., 18 (2001) 327.
15 R. H. Müller, 1996. Zetapotential und Partikelladung in der Laborpraxis. Wissenschaftliche Verlagsgesellschaft mbH Stuttgart, p. 254
16 G. Rytwo, Y. Gonen, S. Afuta and S. Dultz, Appl. Clay Sci., 28 (2005) 67.
17 Y. Xi, W. Martens, H. He and R. L. Frost, J. Therm. Anal. Cal., 81 (2005) 91.
18 S. Yariv and I. Lapides, J. Therm. Anal. Cal., 80 (2005) 11.
19 S. Yariv, M. Mueller-Vonmoos, G. Kahr and A. Rub, Thermochim. Acta, 148 (1989) 457.
20 P. W. Atkins and J. De Paula, 2002. Processes at Solid Surfaces in Physical Chemistry (7th edition). Oxford University Press, Oxford, pp. 977–1007.
21 D. Sparks, Environmental Soil Chemistry, 1995, Academic Press, pp. 104–109.
22 F. L. Lambert, 2004, http://www.secondlaw.com/two.html#time
23 G. Rytwo and E. Ruiz-Hitzky, J. Therm. Anal. Cal., 71 (2003) 751.
24 P. Aranda, B. Casal, J. J. Fripiat and E. Ruiz-Hitzky, Langmuir, 10 (1994) 1207.
25 J. L. Perez Rodriguez and C. Maqueda, Interactions of Vermicullites with Organic Compounds in: Organo-clay Complexes and Interactions. Eds S. Yariv and H. Cross, Marcel Dekker Publ. 2002, p. 139.
26 S. Nir, T. Undabeytia, D. Marcovich, Y. El-Nahhal, T. Polubesova, C. Serban, G. Rytwo, G. Lagaly and B. Rubin, Environ. Sci. Technol., 34 (2000) 1269.
27 S. H. Lee, D. I. Song and Y. W. Jeon, Environ. Technol., 22 (2001) 247.

DOI: 10.1007/s10973-005-7187-5