



Research paper

Physico-chemical characterization of lake pigments based on montmorillonite and carminic acid



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ABSTRACT

Hybrid materials based on one organic dye, the carminic acid, and montmorillonite have been prepared and characterized by a multi-technical approach. Aluminum and tin II cations were used in the experimental mixtures in order to have a chelating effect with the carminic acid. X-Ray diffraction patterns (XRD) did not highlight any intercalation of the organic molecule in the interlayer space, a result confirmed by transmission electron microscopy (TEM) micrographs. The fixation of the organic molecules on the phyllosilicates was then investigated by ¹³C solid state nuclear magnetic resonance (NMR) and time resolved fluorescence spectroscopies. The spectra showed the role that the ketone and catechol functions of the dye played for its fixation and stressed on the decrease of its mobility when the lake pigment was formed. The role of the clay edges and/or surface was highlighted by this set of experimental data.

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1. Introduction

Since Antiquity, precipitating or adsorbing an organic dye onto an inert inorganic substrate was the chemical way used by craftsmen to synthesize new pigments called lake pigments. These chemicals played a very important role on the palette of the artists because of their multiple pink, red or purple shades (Saunders and Cupitt, 1994). The question of their stability is a long standing one to which the answer is very complex and requires experimental investigation on model materials and their characterization before and after fading by different physico-chemical methodologies.

A common phenomenon observed on the paintings is the photodegradation of the dyes. Among the later, carminic Acid (CA, or Cochineal) is a food colorant and one of the oldest coloring agents known in human history; it is a natural product, but it was also obtained synthetically since the 1860s. It was commonly used by painters in the form of Al-based Lake, obtained by its reaction with an aluminum hydrate or sulfate and giving very stable color (Pozzi et al., 2014). In pure form the CA was known to be vulnerable to thermal and photodegradation. Therefore, investigations of the coloration and color degradation mechanisms as function of the dye molecular structure as well as of the matrix effects on coloration stability are important to improve the

conservation of artworks as well as to have a better understanding of the advancements in lake pigment designs (Nevado et al., 1995).

A well-known example of the preservation of the color of a dye-based pigment is the “Maya Blue”. In 1931, Mayan artworks from the 6th century were found on the Yucatan peninsula. The paintings, for the most part, had completely lost their color, but in some areas, a very vibrant blue was found to be nearly completely intact. Mayans had combined indigo, derived from the leaves of the local *añil* plant, with the clay mineral palygorskite, producing a hybrid compound that has conserved its color up to this day. It is interesting to note that (a) indigo that is not bound to clay mineral photodegrades, and (b) indigo bound to other clay minerals similar to palygorskite (e.g., sepiolite) yield a compound that is considerably less stable than the original “Maya Blue” (Sánchez et al., 2006). In the past decade, an increasing number of studies have been devoted to the preparation of dye-clay or silica hybrid materials to understand interactions between inorganic and organic part and to prepare composites similar to Maya blue (Dobrogowska et al., 1991; Yariv et al., 1991).

Stabilization and immobilization of organic dyes on inorganic bases have been already reported in the field of depollution especially (Murata et al., 2000; Murata et al., 2001; Ibarra et al., 2005; Baskaralingam et al., 2006; Loera et al., 2006; Baskaralingam et al., 2007; Lima et al., 2009). Different hosts have been employed: layered double hydroxides (Mg,Zn-Al-O LDH's), gamma-alumina, silica, doped and grafted silica, zeolites and organo-modified clay minerals. A larger number of papers already deals with Methylene Blue-like

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dyes: porphyrin@AlPO₄-5 (Ehrl et al., 1994), phthalocyanine derivative@AlPO₄-55 (Ehrl et al., 1994), thiazine@faujasite63, azo dye@faujasite (Schneider et al., 2000), oxonine, pyronine and oxazine in zeolite L (Pauchard et al., 2000; Pfenniger and Calzaferri, 2000, Megelski and Calzaferri, 2001, Calzaferri et al., 2003; Maas et al., 2003), thionin@mordenite (Simoncic et al., 2004), methylene blue in AlPO₄ (Wohlrab et al., 1992), indigo and quinizarin in faujasite, oxazine@AlPO₄-5 (Seebacher et al., 2003),....

It has been reported also that in dye–clay mineral complexes, interactions between the oxygen plane of the aluminosilicate layer of the clay mineral and the aromatic parts of the dyes occurred (Yariv et al., 1991; Mintova et al., 2015). Metachromasy of methylene blue adsorbed on natural montmorillonite has been previously reported, where it was suggested that when the amount of dye is relatively low compared with the adsorption capacity of the clay mineral, this kind of interactions occurred.

Therefore, by combining the color of natural or synthetic dyes and the resistance of inorganic structures, it is possible to get hybrid materials with improved chemical properties and higher stability. The immediate goals of this work were to understand interactions between the specific dye carminic acid and montmorillonite. Two key parameters have been varied during the preparation of the composites: the nature of the cation associated to the clay mineral and the pH. Ca²⁺, Al³⁺ and Sn²⁺ cations have been used for their capacity to form complexes with OH and carboxylate moieties present in the organic dye. The natural pH was acid around 3.7, sodium hydroxide was added to obtain a neutral one. A multi-technical approach for the characterization has been used and more specifically X-ray diffraction (XRD), Transmission electron microscopy (TEM), ¹³C solid state nuclear magnetic resonance (NMR) and Time-resolved fluorescence.

2. Experimental part

2.1. Montmorillonite synthesis

Reagents were mixed in the following order: deionized water, hydrofluoric acid, sodium fluoride, and sources of interlayer cation, Mg, Al and Si. The use of fluoride allows us to obtain a better crystallinity of the final product (Reinholdt et al., 2001). The hydrogels were matured over a 2 h period at room temperature and then introduced into a PTFE-lined stainless steel autoclave. The autoclaves were heated at 200 °C for 72 h. After reaction, autoclaves were cooled to room temperature under a stream of water. Run products were then recovered by filtration, washed thoroughly with distilled water and dried at 60 °C for 12 h. The ideal formula per half unit cell is Na_{0.2}(Si₄)(Al_{1.8}Mg_{0.2})O₁₀(OH,F)₂ with a theoretical octahedral substitution rate (i.e. the number of Mg²⁺ to Al³⁺ substitution per half-cell) of 0.2, yielding a cation exchange capacity of 0.382 meq·g⁻¹.

2.1.1. Cation-exchange montmorillonite

Before dye adsorption, montmorillonite was exchanged with calcium cations (Ca–Mt) via a procedure described elsewhere (Li et al., 2012). For the exchange procedure in presence of aluminum and tin, aluminum chloride and tin chloride solutions were used at a concentration of 0.1 mol·L⁻¹. In the case of tin solutions, HCl 0.1 M was used. The choice of the later concentration was governed to reach the stability domain of Sn²⁺ and then allow for the cation-exchange process to occur.

The clay mineral was added in a large amount of the cation solution and kept under stirring. A ratio of 1.5 g of montmorillonite for 250 mL of solution was chosen. Three successive baths of increasing times were conducted, 1 h, 3 h, and 24 h, following by centrifugation and five washing steps with water. The solid fraction was dried in an oven at 60 °C.

2.1.2. Dyeing procedure

After mixing with aluminum and tin cations, the montmorillonite (Al–Mt and Sn–Mt) was dyed with carminic acid. Three ranges of pH conditions were chosen, acid, neutral and basic. The acid one resulted of the natural pH of the mixture without correction. For each sample, an amount of 15 mg carminic acid in 25 mL of distilled water was added to 135 mg of montmorillonite loaded cation, or 10% in weight. The solid powder was immediately dispersed under stirring. After 4 h of equilibration, the solid phase was then separated from the solution by filtering and dried at 70 °C overnight.

3. Characterization

XRD was carried out with a diffractometer developed in the laboratory and based on a CuK_{α1} Xenocs Source (wavelength $\lambda = 1.5404 \text{ \AA}$). XRD patterns were recorded between 3 and 50° with a 2D detector (image plate read by a Denoptics scanner). Thermogravimetric analysis (TGA) of the samples was carried out on a TA Instruments, SDT Q600 analyzer with a heating rate of 5 °C min⁻¹ under dry air flow (100 mL min⁻¹). TEM study of the samples was performed on a JEOL100CX microscope. Samples in the form of bulk powders were suspended in ethanol and then deposited on 400 mesh copper grids covered with an ultrathin carbon membrane of 2–3 nm thickness. X-ray fluorescence (XRF) analyses were conducted with an energy dispersive spectrometer developed by LAMS (with a Pd Moxtek Bullet source and a Amptek SDD detector). ¹³C MAS NMR spectra were obtained on a Bruker Avance 500 spectrometer operating at $\Omega_L = 500 \text{ MHz}$ (¹H) and 125 MHz (¹³C). Proton cross-polarization (CP-MAS) was applied with a contact time of 1 ms. Samples were spun at the magic angle at a frequency of 10 kHz. The ¹³C pulse length was 5 ms (close to $\pi/2$), and the recycle delay was 5 s.

Time-resolved fluorescence measurements were performed by the time-correlated single-photon counting technique on carminic acid in water solution and on clay suspensions (Balme et al., 2006). The excitation wavelength was achieved by using a SuperK Extrem high power white supercontinuum laser (NTK Photonics, model EXR-15) as a continuum pulsed source; the wavelength was selected by coupling to a monochromator (Jobin–Yvon H10). The repetition rate was set to 38.9 MHz; the excitation pulse duration on this device is around 6 ps (full-width-at-half-maximum, FWHM). The emission of fluorescence is detected, after passing through a polarizer oriented parallel, perpendicular or at the magic angle (54.73°) to polarization of excitation, through a double monochromator Jobin–Yvon DH10 on a hybrid PMT detector HPM-100-40 (Becker & Hickl). The instrumental response function of the equipment was measured by using a dilute suspension of polystyrene nanospheres in water (70 nm of diameter) as a scattering solution; it was typically about 130–160 ps FWHM. Decays were collected at a maximum count rate of 15 kHz into 4096 channels using an acquisition card SPC-730 (Becker & Hickl). This limiting count rate was achieved by dilution of the sample and after sedimentation of the suspension in order to minimize as much as possible the scattering of the particles. The time per channel was set around 6 ps·ch⁻¹ in order to fit a full decay in the experimental time window. All decays were collected so as to have at least 1.5×10^6 counts in total. Decay analysis was performed using a Levenberg–Marquardt algorithm. For the analysis, the fluorescence decay law at the magic angle $I_M(t)$ was assumed as a sum of exponentials. Fluorescence lifetimes were calculated from data collected at magic angle by iterative adjustment after convolution of a pump profile (scattered light) with a sum of exponentials. We assumed a Poisson distribution of counts in the calculation of the χ^2 criterion; residuals profiles and autocorrelation function as well as Durbin–Watson and skewness factor were used in order to estimate the quality of the adjustment. The number of exponentials used for the fit was increased until all the statistical criterions were improved.

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