From environmental remediation to artworks

A rescue of colors from dye-wastewater

Abstract Contaminants such as dyes unproperly discharged in the environment are a big problem to overcome. Some technologies have been developed and applied for dye-wastewater treatment before its disposal in the waterbodies. Among them, adsorption is highlighted and a plenty of adsorbents are proposed in the literature. This paper presents some clay minerals-based adsorbents applied for the rescue of colors from dye-wastewater, and the development of new pigments for artworks as an alternative to reuse the dyed adsorbents.

Keywords **Dyes, adsorption, clay minerals-based solids, pigments, photostability.**

Résumé **De la dépollution environnementale aux œuvres d'art, ou comment réutiliser les couleurs des eaux usées de teinture**

Les contaminants, tels que les colorants évacués de manière inappropriée dans l'environnement, constituent un grave problème à résoudre. Certaines technologies ont été développées et appliquées pour le traitement des eaux de teinture avant leur élimination dans les plans d'eau. Parmi ceux-ci, les processus d'adsorption sont mis en évidence et de nombreux adsorbants sont proposés dans la littérature. Cet article présente certains adsorbants à base d'argile appliqués pour la récupération des couleurs des eaux usées de teinture, ainsi que le développement de nouveaux pigments pour œuvres d'art comme alternative à la réutilisation des adsorbants colorés.

Mots-clés **Colorants, adsorption, solides à base d'argiles, pigments, photostabilité.**

Dyestuffs and the color paradox

The use of dyes is very wide and ancient in the world. These dyestuffs are present in many products such as foods, drinks, cosmetics, paintings, clothes, medicines, and confers color to different issues. On the other hand, when the residual dyes from any industrial source are discharged into an aquatic body, color is also conferred. Their presence into the natural water resources may make difficult the sunlight passage and become unfriendly to aquatic life. Furthermore, many of dyes or their decomposed sub-products are toxic, carcinogenic or mutagenic to life-forms mainly due to the presence of benzidine, naphthalene or other aromatic compounds [1-2].

Dyes can be applied in a wide range of manufacturers such as textile industries, paper and pulp industries, dye and dye intermediates industries, pharmaceutical industries, tannery, and Kraft bleaching industries, etc. Actually, the major source of aquatic pollution by dyes comes from textile industries. The chemical nature of textile dyes is depending of the chemical structure. *Table I* shows the chemical classification groups determined as azo (–N=N–), carbonyl (C=O) (including anthraquinones), phthalocyanine, aryl carbonium ion (including triphenylmethanes), indigoid, sulfur and nitro chemical classes. Among them, azo dyes constitute the first most important class of textile dyes, followed by anthraquinone dyes. While azo dyes are mostly used for yellow, orange and red colors, anthraquinone dyes are most commonly used for violet, blue and green colors [3].

Modern textile dyes have two keys components: chromophores (which confer colors) and auxochromes (influence hue and solubility of the dye in water and give enhanced affinity to attach with the substrate). Typical chromophores include aromatic rings (benzene, naphthalene or anthracene) and other binding chromophores with double bonding such as azo group (-N=N-), ethylene group (=C=C=), carbonyl group (=C=O), carbon-nitrogen (=C=NH; -CH=N-), and carbon-sulphur (=C=S; ≡CS-S-C≡). The auxochrome groups are ionizable and usually are: $-NH_2$ (amino), -COOH (carboxyl), $-SO_3H$ (sulphonate) and -OH (hydroxyl) [1-2].

The colors of dyes have a strict relationship with the electromagnetic spectrum. It is known that the human eye can normally detect radiations between the wavelengths of 380 and 720 nm [3, 5]. Thus, the colors we perceive for the dyes exhibit a visible range in the electromagnetic spectrum.

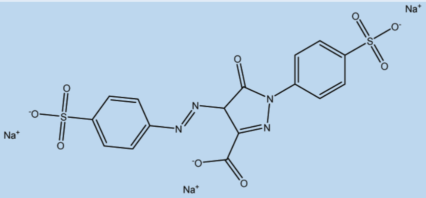
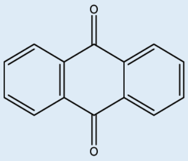
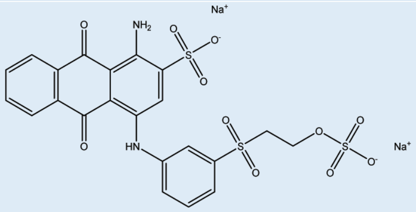
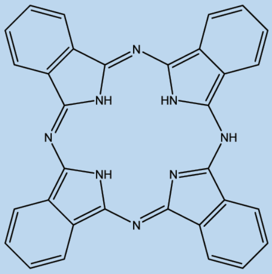
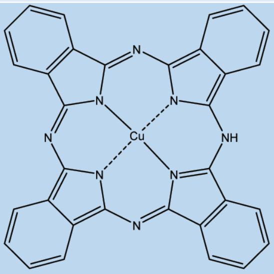
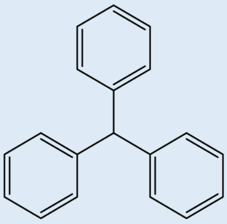
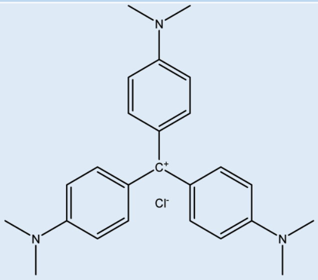
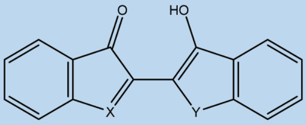
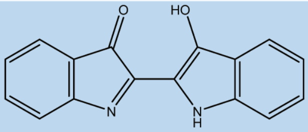
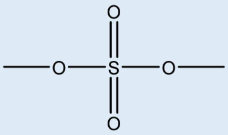
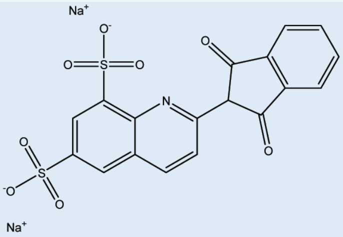
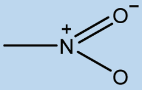
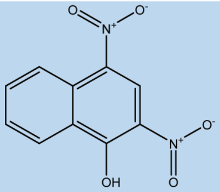
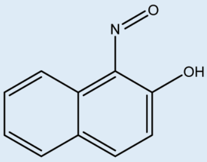
Although dyes make the world more colorful, without adequate treatment, these chemicals can remain in the environment for a long period and cause a serious environmental problem. For instance, the half-life of hydrolyzed Reactive Blue 19 is about 46 years at pH 7 and 25 °C [5-6]. Thus, a huge problem emerges and urges for new technologies to remediate this environmental issue.

How to remove color from dye-wastewater?

Color in water and other liquids is classified in terms of true color and apparent color. True color is the color after particulate matter has been removed (turbidity-free), and apparent color is the one measured without previous treatment [5]. Different techniques based on physical, chemical and biological processes are often described for color-free wastewater discharge (*figure 1*). However, a combination of these processes may be more suitable to meet the requirements than each process alone [6].

Some advantages and drawbacks follow the decolorization methods described in *figure 1*, and their selection will depend on the wastewater characteristics. Due to its simple use and relative low cost, adsorption is highlighted as the most applied as non-biological decolorization processes applied to textile wastewaters. However, the destination of the final solid is still a big challenge to overcome.

Table I - **Some classification of dyes based on chemical structure** [1-2, 4].

CLASS	CHROMOPHORE	EXAMPLE
Azo dyes	$-N=N-$	 Tartrazine
Anthraquinone dyes		 Remazol blue RN
Phthalocyanine dyes		 Phthalocyanine copper (II) (β-form)
Triphenylmethanes dyes		 Cristal violet
Indigoid dyes		 Indigo
Sulfur dyes	 $-O-S(=O)_2-O-$	 Acid yellow 3
Nitro dyes	 $-N^{+}(=O)O^{-}$	 Acid yellow 24
Nitroso dyes	$-N=O$	 1-Nitroso-2-naphthol

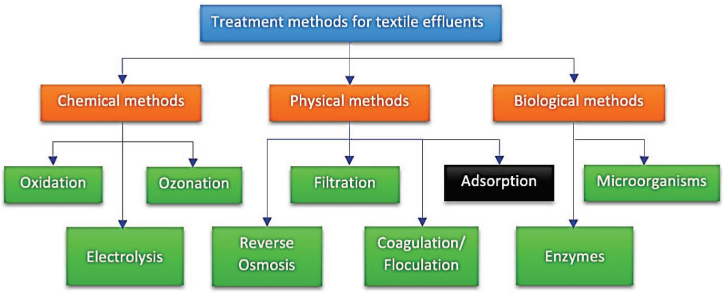


Figure 1 - Treatment methods for the removal of dyes from wastewater effluent. Adapted from [7].

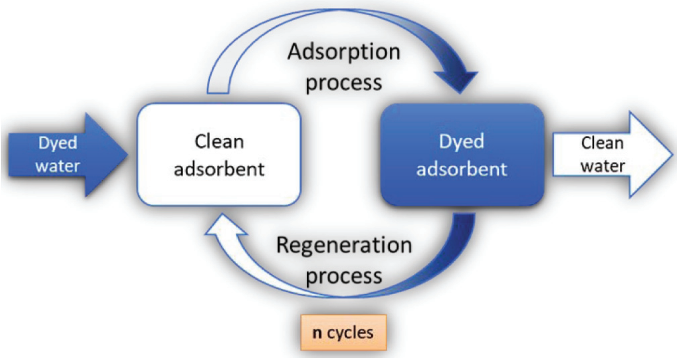


Figure 2 - Adsorption process with adsorbent regeneration step for dyed-water decoloring.

The adsorption approaches

It is known that dyes can be neutral or charged species, then their chemical structures will be important to design of specific solids for their removal. The process of dye removal occurs in a solid/liquid interface and adsorption occupies a prominent place. Therefore, the production of new surfaces for dye interaction is highly dependent of the nature of the dye and the wastewater. Then a custom-made solid involves steps of synthesis and characterization, including the nanometric scale, before application.

Usually, the adsorption study is performed by using the batch technique to obtain equilibrium data. The processes depend of the dye and the solids but also of different experimental conditions as adsorbent dosages, pH, times of contact, initial concentrations of the dye and temperature. The procedure involves the evaluating of the data by experimental isotherms which are modelling to theoretical kinetic and equilibrium isotherms.

Figure 2 shows a typical adsorption process of dye-wastewater discoloration. In this system, clean adsorbents act rescuing the color from dyed-water and stabilizing dyes by physical and/or chemical sorption under solid/liquid interface. This process leads to "clean" water. In their turn, dyed adsorbents may also be regenerated and run other adsorption cycles, depending on their regeneration capacity and stability under the recovery process.

The amount of dye in solution is normally quantified by UV-vis spectrometry at the maximum dye absorption wavenumber. By the difference between the initial (C_0) and final (C_f) dye concentration in a volume of solution (Vs) and a certain mass content of the clay mineral (m), the amount of removed dye is obtained [8]: $q = (C_o - C_f).Vs/m$.

A required point in this study is the characterization of the final solid to determine the principal solid/dye interactions and, therefore, to improve the properties of the adsorbents for any specific dye.

How to characterize the adsorbents?

Once the solids are prepared, the use of characterization techniques for solids is necessary to understand the surface modification. Various methods can be pointed out to evaluate the chemical composition, chemical anchored groups, changes in the textural properties and morphology of the particles as summarized in *figure 3*.

Custom-made clay-based solids for dye removal

Among a plenty of adsorbents available, clay and clay minerals are highlighted, and we will focus on them from now. Their physical-chemical properties, relative abundance and low-cost

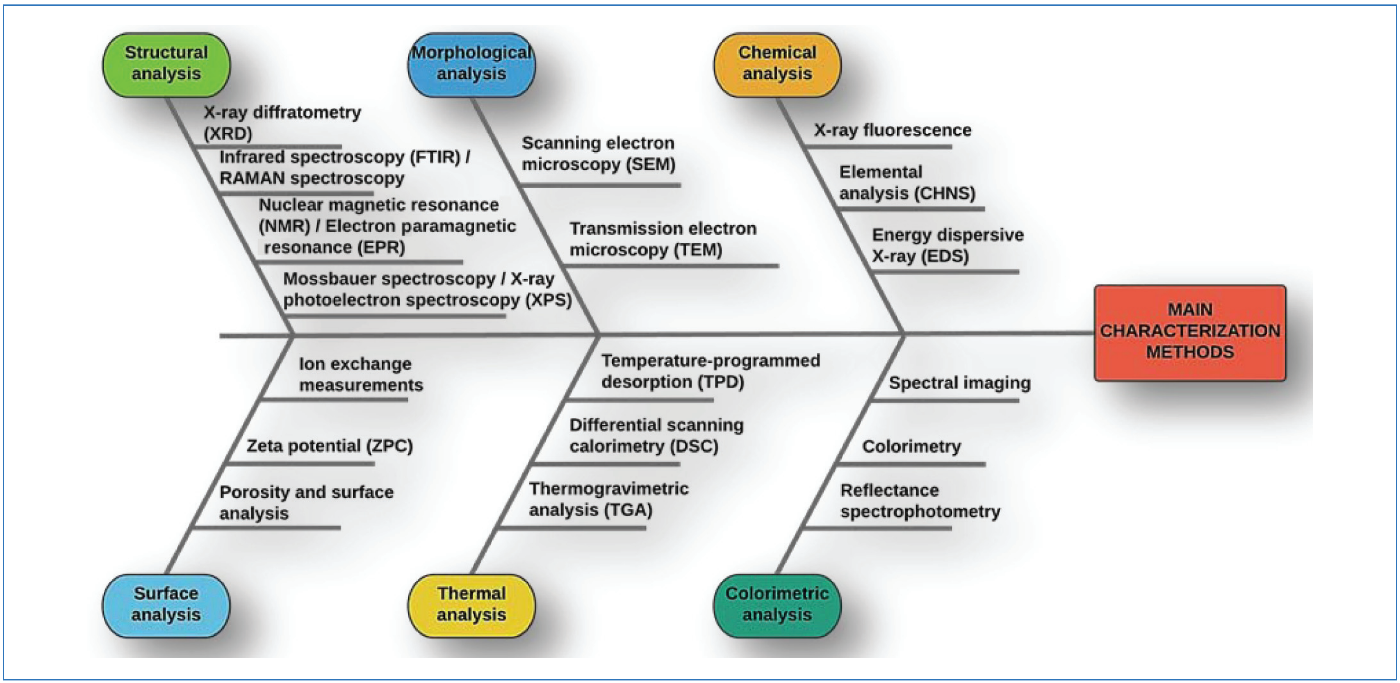


Figure 3 - Main analytical techniques for characterization of adsorbents.

allow them as potential adsorbents for dye recovery from wastewaters. Three relevant characteristics of clay minerals in this field are their specific area, their ion exchange capability and the possibility of physical-chemical modification on their surface.

The negative charged clay surfaces and their ion-exchange sites allow them to associate directly with cationic dyes such as methylene blue and thiazine blue. Although other types of chemical forces can occur, the electrostatic interaction between the species is preponderant. Methylene blue/clay minerals is a classic topic of research, and various adsorbents based on clay minerals have been developed using methylene blue as a probe molecule.

Although some clay surfaces present naturally sites for dye accommodation, further modifications may be necessary to improve the dye removal from wastewater. The modification of clay surface involves a large number of chemical, physical or combination of procedures based on top-down (post-synthesis methods) or bottom-up approaches including the use of organic or inorganic ensembles: intercalation, ion exchange, pillarization, etc. The use of discrete organic neutral molecules such as amino acids, amines, charged organic species (ammonium derived from quaternary ammonium salts) or large molecules as biopolymers, proteins is widely studied.

In the literature, functionalized clay minerals and clay-based composites are widely used as adsorbents for dye-wastewater. Clay-based adsorbent are obtained by replacing the original exchanged cations with organic compounds such as alkylammonium derivatives resulting in organic-inorganic hybrid materials. In its turn, clay-based composites are mainly prepared with polymers or biopolymers, such as chitosan. *Table II* summarizes some clay-based adsorbents as examples for Remazol blue dye removal.

Table II - Examples of clay and clay-based solids as adsorbents for Remazol blue dye.

ADSORBENTS	CONDITIONS	REMOVAL CAPACITY (mg g^{-1})	REF.
Montmorillonite-dodecylamine	50 mg, pH 4, 40 min, 100 ppm	39	[9]
Bentonite/3-aminopropyltrimethoxysilane-EG	50 mg, pH 2, 50 min, 100 ppm	107	[10]
Bentonite/C14-200%CEC	75 mg, pH 7, 60 min, 300 ppm	211	[11]
Bentonite/C16-200%CEC	100 mg, pH 7, 60 min, 300 ppm	163	
Bentonite/C18-200%CEC	75 mg, pH 7, 60 min, 300 ppm	287	
Montmorillonite	50 mg, pH 3, 60 min, 800 ppm	0	[12]
Chitosan-montmorillonite (5%m/m)	50 mg, pH 3, 480 min, 800 ppm	335	

Silva and co-workers prepared intercalated hybrid materials based on KSF-montmorillonite and protonated dodecylamine for Remazol brilliant blue dye removal [9]. The adsorbents were characterized by using CHN elemental analysis, thermogravimetry and FTIR spectroscopy. Some adsorption effects, such as the dosage of adsorbent, contact time, initial dye concentration, pH and temperature were evaluated. Both kinetic and thermodynamic parameters of the adsorption process were obtained. The adsorption process revealed an exothermic and spontaneous reaction and the data were well-adjusted to the pseudo-second-order model. The results showed that functionalized montmorillonite improves the anionic dye removal from aqueous solution (*figure 4*).

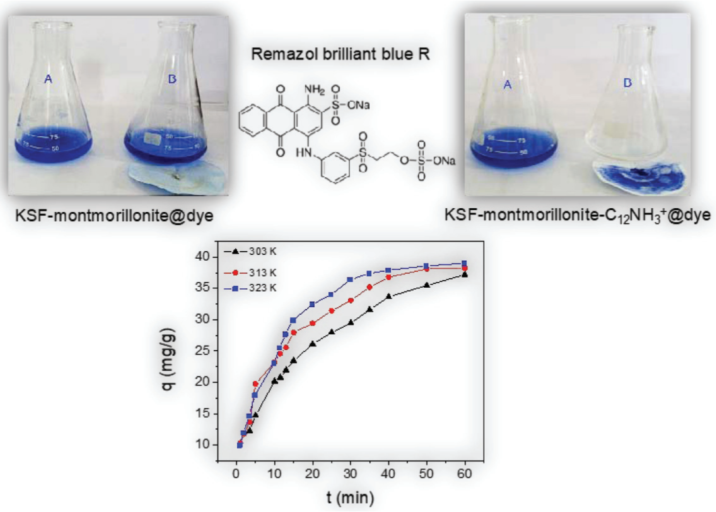


Figure 4 - Effect of the time in the dye removal for KSF-montmorillonite-$C_{12}NH_3^+$ hybrid. Adapted from [9].

The prepared charged amino-montmorillonite was used for dye removal; however, the adsorption capacity is not higher as other adsorbents. Among other strategies for chemical modification of clays, a composite with polymers may appear attractive. The clay properties associated to the polymer ones may act in a synergic way and result in composites with improved properties. As example, montmorillonite-chitosan composites have been prepared and applied for dye removal [12]. Chitosan is a biopolymer obtained from the deacetylation reaction of chitin, a second biopolymer more abundant in the world. In this way, a green biosorbent is proposed as an alternative to dye removal from wastewaters.

In order to improve the pH stability of chitosan in acid medium, chitosan-clay beads have been synthetized and the clay content was also investigated. The use of beads is important for adsorption because at the end of the process, a facile recovery of the solids is possible by filtration. In this context, Pereira and co-workers prepared KSF-montmorillonite/chitosan beads by using a commercial montmorillonite (KSF) and sodium tripolyphosphate as crosslinking agent [12]. This work shows the increasing of montmorillonite content from 1 to 25 % leads to an improvement of composite properties. Remazol blue RN dye was used as anionic dye probe in different conditions at pH (2-8), contact time (0-660 min) and dye concentration (100-1600 mg L^{-1}). The results were very promising and suggested the prepared adsorbents to remove anionic dyes from wastewater even in acidic medium. Furthermore, this modification has made montmorillonite available to anionic dyes adsorption (*figure 5*).

Although chitosan/montmorillonite beads presented high dye removal capacity, the equilibrium was reached for long times. This fact may increase the dye removal process costs and the use of this adsorbent should be well-evaluated.

Other example of modified bentonite (Bent, a rich montmorillonite clay) is concerned to alkyl ammonium clays obtained using three cationic surfactants tetradecyl- (C14), hexadecyl- (C16) and octadecyl-trimethylammonium (C18)

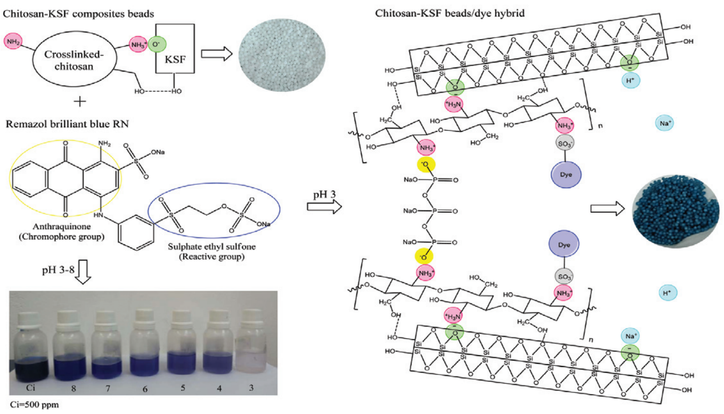


Figure 5 - KSF-montmorillonite/chitosan beads as adsorbent for Remazol blue dye. Adapted from [12].

bromides by using ammonium salts at 50 °C for 5 min over microwave heating [11]. The ammonium salts were used in the proportions of 100 and 200 % of the cationic exchange capacity [13] of the clay sample. The solids were applied for Remazol blue RN dye removal from a single and synthetic effluent sample. The influences of the pH, adsorbent dosage, contact time and initial dye concentration were investigated. The adsorption data were fitted to pseudo-second order and Langmuir models. The maximum retentions were 195, 199 and 209 mg g^{-1} for Bent-C14-100 %, Bent-C16-100 % and Bent-C18-100 %, as well as 211, 163 and 287 mg g^{-1} for Bent-C14-200 %, Bent-C16-200 % and Bent-C18-200 %, respectively, at 60 min and pH 2.

The organobentonites were also used in a simulated dye effluent containing tree Remazol dyes and a mixture of inorganic salts. For all of the hybrids, the absorbance in the monitored wavelength (λ_{max} = 412 nm, Remazol yellow GR dye; λ_{max} = 540 nm, Remazol red RB dye; and λ_{max} = 609 nm, Remazol blue RN dye) decreased significantly after adsorption. The best results were found for Bent-C14-100 % and Bent-C14-200 %, with removals close to 98 and 99 %, respectively. Bent-C16-200 % and Bent-C18-200 % hybrids presented less efficiency to remove all of the dye in the mixture; however, both hybrids were selective for Remazol yellow GR, which has a maximum absorbance at 412 nm.

Although increasing the amount and the length of organic alkyl chain for hybrids prepared with 100 and 200 % of the CEC did not result in a higher efficiency of the solids, the organosolids have shown good performances for dye removal from aqueous solution. The change in the surface charge of organobentonites contributed to high Remazol blue RN removal as well as good removal of the dyes in the synthetic effluent.

The aforementioned examples illustrated the use of three different synthetic routes for the synthesis of amino modified clay minerals and the improvement of the designed surfaces to work at solid/dye interface. However, the research in field of dye/solid chemistry is wide and not only for development of new adsorbents with high performance and selectivity.

What about the adsorbents after dye removal? How to discharge them?

A big problem involving adsorption processes for environmental remediation is related to the final solid destination. Some processes may involve waste incineration, chemical desorption, photodegradation, etc. However, they also need additional treatment to not release contaminants or subproducts in the environment that sometimes are more aggressive than the original dye.

Although the literature has proposed a plenty of adsorbents for dye removal, the discharge of the dyed adsorbents is usually neglected. Thus, new technologies to treat or to reuse this special trash is highly desired.

Dyed adsorbent as new pigments

Findings on applied clay science discussed by French researchers from Sorbonne University in Paris prepared lake pigments based on montmorillonite dyed with carminic acid and characterized by a multi-technical approach [14]. The nature of the cation associated to the clay mineral and the pH were investigated as key parameters in the preparation of the hybrids. Aluminum and tin(II) were used as exchanged cations in calcium-montmorillonite in order to evaluate the chelate effect with the organic dye. *Figure 6* evidenced that colors of the hybrid materials were pH dependent and varied based on the pKa's of the carminic acid (3.1, 5.9 and 8.1). Furthermore, the nature of the cation associated to the clay mineral and the amount of retained organic matter were also evidenced. The results showed the dye removal capacity and the intensity of colors followed the order: tin-montmorillonite > Al-montmorillonite > Ca-montmorillonite.

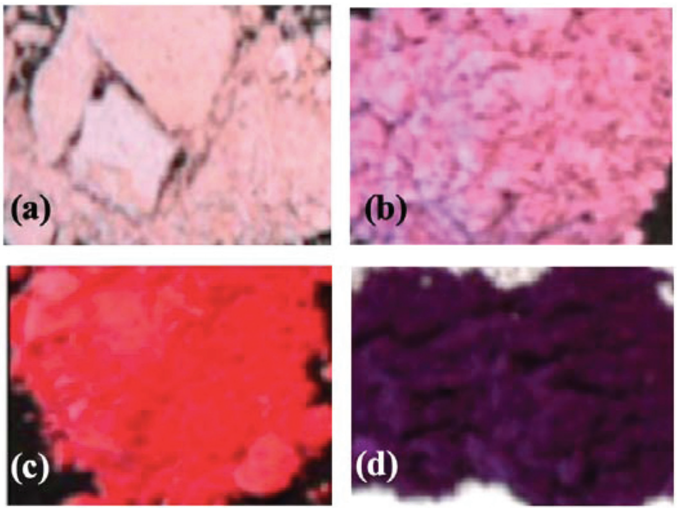


Figure 6 - Color variation of the hybrids as a function of the exchanged cation: (a) Ca-Mt-carminic acid; (b) Al-Mt-carminic acid pH 3.7; (c) Al-Mt-carminic acid pH 7.0; and (d) Sn-Mt-carminic acid. Adapted from [14].

Following the steps of development of clay-based pigments, the same French group makes arrangements with a Brazilian group of researchers to prepare new pigments. They developed some hybrid pigments by stabilization of organic dyes onto Ti- and Al-pillared montmorillonite [15]. Carminic acid (CA) and alizarin (Aliz) were used as colorants. Researchers point out carminic acid and alizarin as indigo-type dyes with archeological interests. Results showed that different parameters such as pH, the amount of the adsorbed dyes and the nature of metallic cations in the interlayer space had influenced the color and hue of the hybrids. Oil paint formulations were prepared to simulate real inks applied for oil-based paintings. Although both lake pigments showed stable under light exposure, the pigments based on Al-pillared

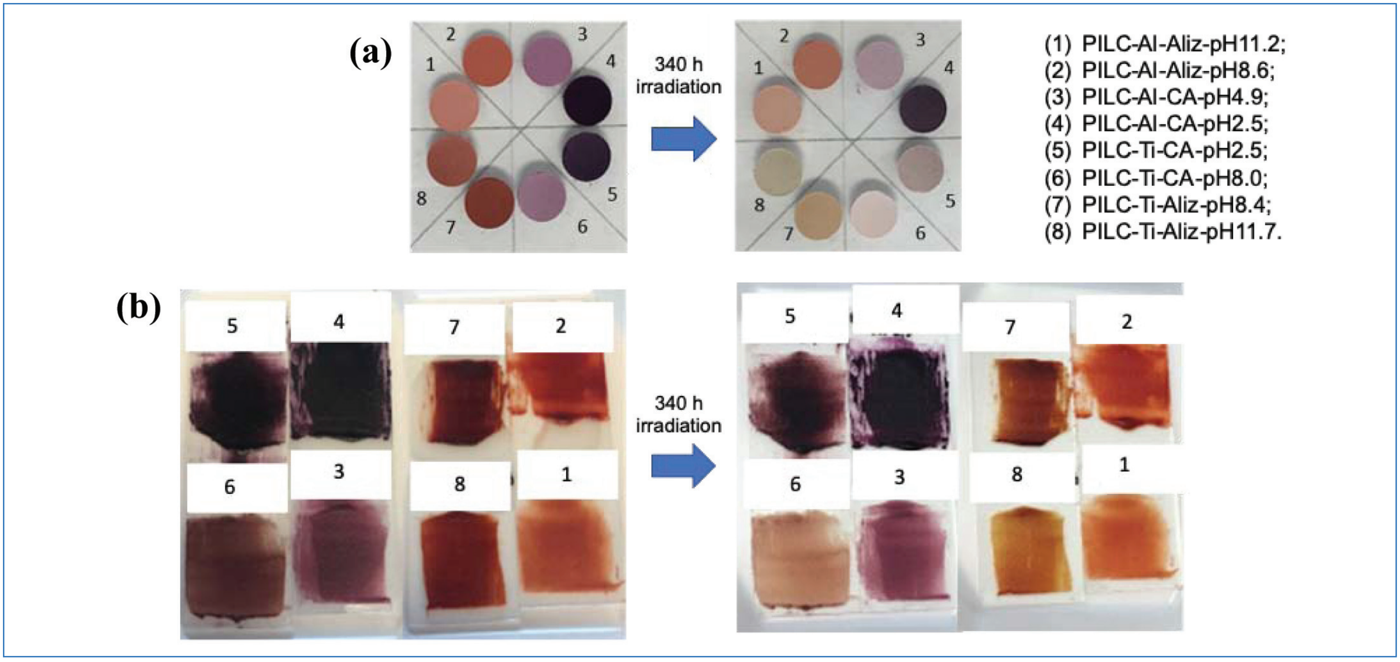


Figure 7 - Solid pigments based on alizarin and carminic acid adsorbed onto Al-pillared clay and Ti-pillared clay (a) and oil paint formulations based on these pigments (b) before and after light irradiation. Adapted from [15].

montmorillonite (PILC-Al) were more stable than Ti-based hybrids (PILC-Ti), even in oil painting formulations (*figure 7*).

In order to inverse the montmorillonite surface and to improve carminic acid adsorption, a cationic polymer was applied. Guillermin and co-workers used montmorillonite modified with polydiallyldimethylammonium chloride to prepare lake pigments with carminic acid [8]. Molecular interactions were underlined thanks to spectroscopic characterizations that proposed hydrogen bonding as the main adsorption mechanism between modified clay hybrids and the dye. Different dyed samples were submitted to ageing under light and all fading curves showed close to each other (*figure 8*).

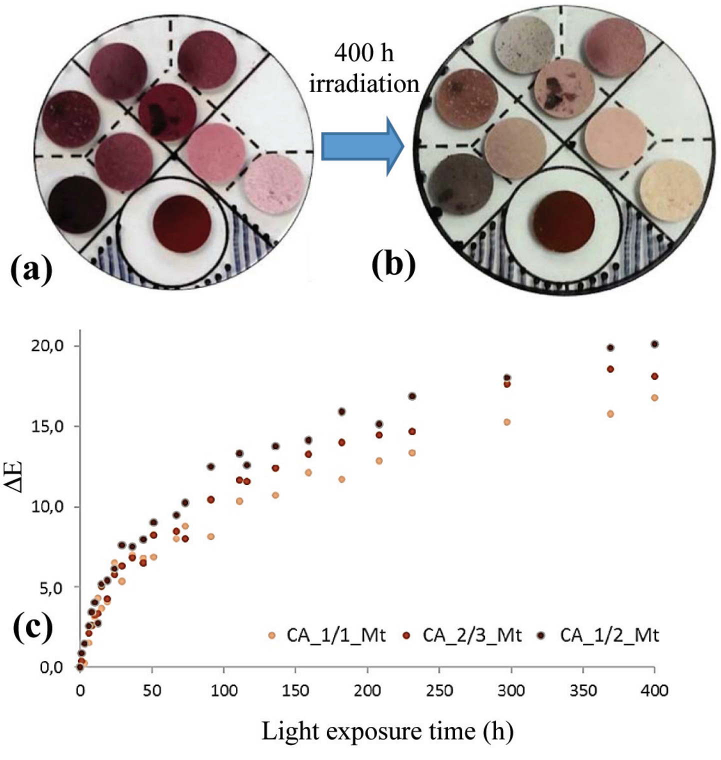


Figure 8 - Color of the pigments before (a) and after (b) 400 h under light exposure. (c) Represented ageing of pigments followed by color change observations. Adapted from [8].

Although the presence of the cationic polymer in the hybrids seemed to prevent the dye from being released in different solvents, it does not affect the photostability of the samples.

Towards new stable and environmentally friendly pigments

The above-mentioned examples showed three different pathways to prepare hybrid pigments based on carminic acid (CA) and/or alizarin (Aliz) onto exchanged-Al(III) and -Sn(II) montmorillonite/CA, Al- and Ti-pillared montmorillonite/CA or Aliz and polydiallyldimethylammonium-montmorillonite/CA. The solid pigments exhibited beautiful quite-stable colors able to prepare ink formulations for paintings. However, the routes to follow the archeological pigments steps are considered under research and other colors should be raised by modifying the inorganic surfaces and the dye-kind to new stable pigments.

Considering again the problematic of dyestuff and the color paradox: if we asked you: "*Do you like colors?*" Your answer should probably be: "*Of course, I do*". But at what cost? Have you ever thought about the amount of clean water necessary to dye your beautiful clothes? And what about the dyed wastewaters from textile industries and the negative impacts from their inappropriate discharge on the environment? Therefore, the rescue of colors from dye-wastewater and the reuse of dyed adsorbents as pigments appear to be a smart way to reduce some environmental problems. Thus, color paradox is solved and the final solids after adsorption are well-destinated. This proposed route minimizes the negative impacts of the improperly discharge of the dyes in the environment and develops high-value technologic products from "trash". Furthermore, the prepared pigments may be applied in different ink formulations for paintings and may help consolidate our cultural heritage from artworks.

As example, Jacopo Tintoretto, (1518-1594), an Italian Renaissance artist, used an aluminum salt with carminic acid (carmine lake) as a pigment to obtain a bright-red color in several of his paintings, including *Christ washing the Feet of*

Figure 9 - *Christ washing the Feet of the Disciples*, an oil painting on canvas performed by Jacopo Tintoretto in 1575-1580. © The National Gallery, London.

the Disciples (*figure 9*). Likewise, new hybrid pigments may be useful to help new artists or to restore great ancient artworks.

[1] Suteu D. *et al.*, Using of industrial waste materials for textile wastewater treatment, *Environ. Eng. Manag. J.*, **2009**, *8*, p. 1097.

[2] Zaharia C. *et al.*, Textile wastewater treatment by homogenous oxidation with hydrogen peroxide, *Environ. Eng. Manag. J.*, **2009**, *8*, p. 1359.

[3] Christie R., *Colour Chemistry*, Royal Society of Chemistry, **2014**.

[4] Rajabi M., Mahanpoor K., Moradi O., Removal of dye molecules from aqueous solution by carbon nanotubes and carbon nanotube functional groups: critical review, *RSC Adv.*, **2017**, *7(74)*, p. 47083.

[5] Dos Santos A.B., Cervantes F.J., van Lier J.B., Review paper on current technologies for decolourisation of textile wastewaters: perspectives for anaerobic biotechnology, *Bioresour. Technol.*, **2007**, *98(12)*, p. 2369.

[6] Hao O.J., Kim H., Chiang P.-C., Decolorization of wastewater, *Crit. Rev. Env. Sci. Tec.*, **2000**, *30(4)*, p. 449.

[7] Saratale R. *et al.*, Bacterial decolorization and degradation of azo dyes: a review, *J. Taiwan Inst. Chem. Eng.*, **2011**, *42*, p. 138.

[8] Guillermin D. *et al.*, New pigments based on carminic acid and smectites: a molecular investigation, *Dyes and Pigments*, **2019**, *160*, p. 971.

[9] Silva M.M.F. *et al.*, Adsorption of an industrial anionic dye by modified-KSF-montmorillonite: evaluation of the kinetic, thermodynamic and equilibrium data, *Chem. Eng. J.*, **2012**, *203*, p. 259.

[10] Fernandes F.M., Baradari H., Sanchez C., Integrative strategies to hybrid lamellar compounds: an integration challenge, *App. Clay Sci.*, **2014**, *100*, p. 2.

[11] Brito D.F. *et al.*, Organophilic bentonites obtained by microwave heating as adsorbents for anionic dyes, *J. Environ. Chem. Eng.*, **2018**, *6(6)*, p. 7080.

[12] Pereira F.A.R. *et al.*, Green biosorbents based on chitosan-montmorillonite beads for anionic dye removal, *J. Environ. Chem. Eng.*, **2017**, *5(4)*, p. 3309.

[13] Pedreira-Segade U. *et al.*, Adsorption of nucleotides onto ferromagnesian phyllosilicates: significance for the origin of life, *Geochim. Cosmochim. Acta*, **2016**, *176*, p. 81.

[14] Fournier F. *et al.*, Physico-chemical characterization of lake pigments based on montmorillonite and carminic acid, *Appl. Clay Sci.*, **2016**, *130*, p. 12.

[15] Trigueiro P. *et al.*, When anthraquinone dyes meet pillared montmorillonite: stability or fading upon exposure to light?, *Dyes and Pigments*, **2018**, *159*, p. 384.

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