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1 **Designing photochromic pigments based on clay minerals and spiropyran**
2

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10
11 **Highlights**

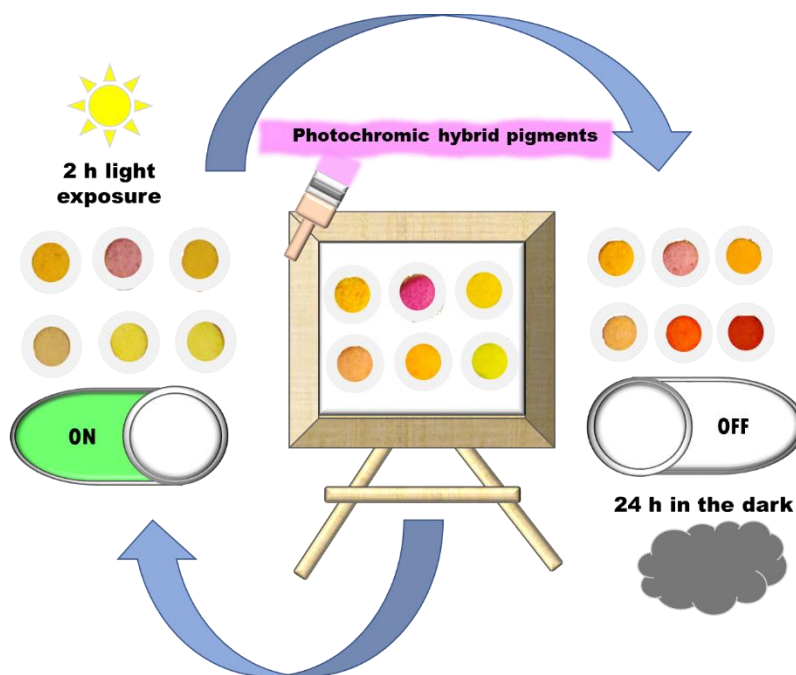
- 12 • Photochromic hybrid pigments were prepared through adsorption of spiropyran on clay
13 minerals.
- 14 • Al-pillared saponite presented high dye adsorption compared to the raw saponite.
- 15 • Pigments' colors are pH dependent.
- 16 • Reversibility of the colors is light dependent.

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28 Graphical Abstract



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32

33 **Abstract**

34 Inorganic-organic photochromic hybrid materials have attracted attention in different
35 research fields, since they have a wide potential application in optical memories, sensors, filters,
36 lenses, pigments, and decoration. In this work, the photochromism of the 1-(2-Hydroxyethyl)-
37 3,3-dimethylindolino-6'-nitrobenzopyrylospiran dye was investigated through the preparation
38 of hybrid pigments based on raw and pillared saponites at pH 2 and pH 13 at 25 °C. The second
39 group of pigments was prepared at pH 2 and 25 °C by in-situ hydrolysis of TEOS in the presence
40 of the same dye. All prepared solids were characterized by X-Ray diffraction, ¹³C CP/MAS
41 NMR and thermogravimetry, and were submitted to irradiation under visible light. The results
42 suggested both intercalation and/or adsorption of the dye onto clay mineral surface via
43 hydrogen bonds for the saponite based pigments. Concerning the hybrids obtained from TEOS
44 hydrolysis reaction, the dye acts as a template resulting in a higher photostability of the resulting
45 pigment compared to those prepared with clay minerals. In general, all hybrid pigments
46 presented photoreversible capacity after light exposure and subsequent time-out in the dark.
47 The findings of this study proposed the multicolored prepared hybrids as promising materials
48 to be applied in photochromic systems as smart pigments.

49

50 **Keywords:** Hybrid pigments, saponite, dyes, photochromic pigments, spiropyran.

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53 **1. Introduction**

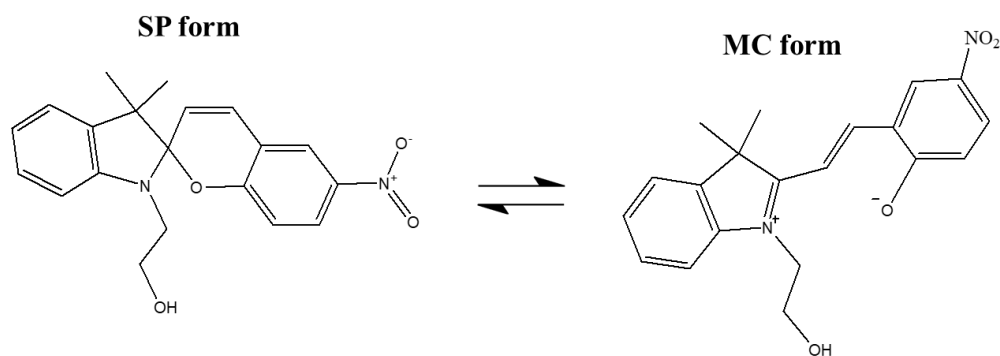
54 Phenomena associated with color variation have been studied in last years in different
55 fields. With regard to pigments, the production of new photochromic materials is highly desired
56 to mimic the occurrence of different types of photochromic transformations observed in nature
57 [1]. Photochromic species present reversible structural transformations over some
58 environmental stimulus including solvents, temperature, presence of metal ions or UV-Vis light
59 irradiation [2,3,4]. The reactivity of the natural systems allows significant changes in the
60 conformation of molecules to occur in response to external stimuli. The latter systems have
61 been inspiring the study and development of new materials with improved properties compared
62 to their isolated form [5,6]. The isomerization caused by light irradiation has advantages
63 associated to the precision and specificity of the molecules, especially if used in light absorption
64 systems [2,3].

65 Structural and electronic changes in the dye after a specific stimulus allow several
66 photosensitive applications. However, the colorants need to have some properties such as
67 thermal stability of the generated isomers, high sensitivity, rapid response and solid state
68 reactivity, which make their use feasible [7].

69 Spiropyrans (SPI) are a class of compounds used in the development of multifunctional
70 materials capable of detection [8]. SPI molecules present a reversible photoconversion between
71 two thermodynamically stable states: a form of spiropyran (SP) and a form of merocyanine
72 (MC) where both forms are structurally different and the resulted chemical properties are also
73 distinct (Figure 1) [9,10].

74

75



76
77

Figure 1- Isomerization between SP and MC forms of the spiropyran structure.

78 Despite the interesting photochromic properties of the spiropyrans, they have limitations
79 associated to thermal stability under radiation [8]. Moreover, previous studies showed that
80 when spiropyran was attached to a planar surface, it increases the resistance to “fatigue”
81 (gradual degradation with increasing number of switching cycles) in comparison to spiropyran
82 molecules in solution [11].

83 Development of photosensitive materials based on SPI has been widely reported
84 [7,12,13]. In general, it is desirable to obtain compounds that retain the SPI's molecular
85 interconversion properties and that have additional light and temperature stability properties
86 [8,14]. The preservation of the properties of some SPI after adsorption on aluminium or silicon
87 oxides surfaces and aluminosilicates was documented in the literature. SPI adsorbed on oxide
88 surfaces presented higher reversibility in comparison to the one observed in solution [15]. Two
89 routes are normally used to prepare photochromic hybrid pigments: the encapsulation of the
90 organic dye in inorganic materials through an in-situ approach and the adsorption of the dye on
91 inorganic minerals [16].

92 Encapsulation can be performed using various techniques such as layer-by-layer
93 assembly and sol-gel method [16–18]. Silica was widely reported for the preparation of hybrid
94 pigments due its transparency and stability. Sol-gel approaches are based on TEOS hydrolysis
95 in an alcohol/water mixtures under acid or basic conditions [19] and the preparation of films

96 was reported to prevent corrosion, and as a barrier for pigments with aluminum in their
97 composition [20,21].

98 The methods of preparing pigments by adsorption on inorganic surfaces are inspired by
99 the ancient Maya Blue composed mainly of palygorskite clay and indigo dye. This pigment has
100 demonstrated extraordinary physical-chemical stability and have attracted attention in research
101 worldwide. The development of mimetic new hybrid stable systems containing inorganic
102 surfaces and colorants are highly desired. In this context, layered solids such as double layered
103 hydroxides [22,23], smectites [24,25], palygorskite [26,27] and sepiolites [28,29] have been
104 applied. Saponite is a trioctahedral 2:1 smectite highlighted as an alternative to prepare hybrid
105 pigments thanks to the presence of active sites on its surface and internal exchanged cations in
106 the interlamellar region that allow interaction with chromophores.

107 In fact, pigments based on raw clay minerals are widely obtained by ion exchange
108 between cationic dyes and interlayer cations of the clay mineral [30]. However, introduction of
109 new functionalities on the clay mineral surface by using organic and/or inorganic modifications
110 are also explored, allowing preparation of new pigments with different chromophores derived
111 from anionic species depending on the desired application [31,32].

112 Immobilization of SPI on inorganic supports has numerous advantages, such as absence
113 or lower leaching, better mechanical properties, higher solubility, biocompatibility [7,33–35]
114 and reduction in the photodegradation of the dye molecule. The latter aspect is related to a better
115 resistance to photoisomerization and less gradual degradation with cumulative switching cycles
116 [7]. Therefore, the preparation of pigments based on interactions of the dye with inorganic
117 matrices such as silicates or other oxides allows protection of the photosensitive species.
118 Moreover, materials with reversible response present unique possibilities for different
119 applications, such as biosensors, chemical sensors, controlled release, data memory systems,
120 thermal and mechanical sensors, among other applications. [36,37]. Among the numerous

121 possibilities provided by SPI, the production of pigments allows the creation of new
122 photochromic systems [35]. Dyes such as nitrobenzopyrane and their analogues have been
123 studied to produce pigments, since they have well-established photochemical properties
124 [12,38,39].

125 In this work, we aimed to synthesize photochromic pigments by using 1-(2-
126 Hydroxyethyl)-3,3-dimethylindolino-6'-nitrobenzopyrylospiran (SPI-H1042; CAS 16111-07-
127 2) immobilized on raw and aluminium pillared saponites. In-situ approach was also used based
128 on TEOS hydrolysis. The resulting pigments were characterized by XRD, thermal analysis and
129 ¹³C solid state NMR. The photoreversibility under light was tested.

130

131 **2. Experimental**

132 *2.1 Materials*

133 The following chemicals were used as received without prior purification: hydrofluoric acid
134 (40% w/w; Fluka), sodium acetate (99%; Sigma-Aldrich), magnesium acetate (99%; Sigma-
135 Aldrich), aluminium oxide (99.8%; Sigma-Aldrich), silica (Aerosil 380; 99.8%; DEGU),
136 aluminium chloride (99%; Sigma-Aldrich), sodium hydroxide (98.9%; Merck), Tetraethyl
137 orthosilicate (TEOS, > 99%, Sigma-Aldrich), 1-(2-hydroxyethyl)-3,3-dimethylindolino-6'-
138 nitrobenzopyrylospiran (SPI; H1042; > 93%; TCI Chemicals), ethanol (95%; VWR) and HCl
139 (37%; Labkem).

140

141 *2.2 Synthesis of raw saponite*

142 Raw saponite was prepared according to a previous methodology [40], having the ideal
143 formula per half unit cell: $\text{Na}_{0.4}[(\text{Si}_{3.6}\text{Al}_{0.4})\text{Mg}_3\text{O}_{10}(\text{OH}, \text{F})_2].n\text{H}_2\text{O}$. The precursor gel was
144 obtained by reagent mixture added in the following order: deionized water (65.38 g; 3.63 mol),

145 hydrofluoric acid (0.38 g; 0.96 mmol), sodium acetate (0.18 g; 2.15 mmol), magnesium acetate
146 (3.46 g; 16.14 mmol), aluminium oxide (0.34 g; 3.33 mmol) and silica (1.15 g; 19.21 mmol).
147 The initial hydrogel presented the following chemical composition 1.00SiO₂: 0.06Al₂O₃:
148 0.83MgO: 0.06Na₂O: 0.05HF: 192.00H₂O. It was kept under magnetic stirring at 25 °C for 4 h
149 and then was transferred to an autoclave and heated at 220 °C for 72 h. Finally, the final solid
150 was washed with deionized water, centrifuged, and dried at 50 °C for 48 h.

151 2.3 *Synthesis of Al₂O₃ pillared saponite*

152 Al₂O₃ pillared saponite was prepared according to an adapted procedure from Bergaoui
153 *et al.* (1995) [41]. Initially, the aluminium pillaring solution was obtained by hydrolysing
154 aluminium chloride with a NaOH solution up to OH:Al ratio of 2.2 and final concentration of
155 Al³⁺ 0.1 mol L⁻¹. The solution was kept under magnetic stirring for 24 h at 25 °C and then added,
156 dropwise, to the aqueous saponite suspension, resulting in a mixture of 7.5 mmol Al³⁺ per gram
157 of clay. The mixture was aged under stirring for 24 h at room temperature. The obtained solid
158 was centrifuged and washed with deionized water and dried at 50 °C for 24 h and then named
159 as Sap-Al. Finally, the Sap-Al sample was calcined at 500 °C for 2 h and the final pillared
160 saponite was designated as PilSap.

161 2.4 *Preparation of the photosensible pigments*

162 Two different preparations were used for the synthesis of the pigments. The first method
163 was based on adsorption on the prepared solids and the second one was the in-situ hydrolysis
164 of TEOS in presence of the dye. In both methods, the amount of SPI was 30 mg (0.085 mmol)
165 for preparation of the hybrid pigments.

166 2.4.1 *Preparation of the pigments by adsorption on Sap and PilSap*

167 The adsorption of spiropyran on saponite and pillared saponite was carried out in acidic
 168 (pH 2) and basic (pH 13) media with predefined amounts of the solids for the preparation of the
 169 hybrid pigments as summarized in Table 1. The dye was initially solubilized in 2.5 mL of
 170 ethanol, then the solid was transferred to the dye solution and 2.5 mL of distilled water were
 171 added. pH of the medium was then adjusted by adding HCl 0.1 mol L⁻¹ and NaOH 0.1 mol L⁻¹.
 172 All systems were stirred for 4 h and then the solids were separated by centrifugation, washed
 173 with ethanol, and dried at 50 °C for 24 h. Pigments were denominated considering mass (suffix
 174 1 for 250 mg and suffix 2 for 1000 mg) and pH (A: acid; B: basic). A fixed amount of 250 mg
 175 was used in all preparations with the pillared saponite.

176
 177 Table 1- Amounts of clay mineral samples used in the preparation of the hybrid pigments in
 178 acid and basic conditions.

Sample	Amount (mmol)	pH
Sap-SPI-A1	0.71	2
Sap-SPI-A2	2.83	2
PilSap-SPI-A	0.71	2
Sap-SPI-B1	0.71	13
Sap-SPI-B2	2.83	13
PilSap-SPI-B	0.71	13

180

181 2.4.2 Synthesis based on hydrolysis of TEOS

182 Pre-hydrolysis of TEOS was performed in 2.5 mL of water with specific amounts of
 183 silane, 12 and 24 mmol for TEOS-SPI-1 and TEOS-SPI-2 pigments, respectively. Pre-
 184 hydrolysis solution was kept under stirring for 24 h at 25 °C. Subsequently, SPI (0.085 mmol)
 185 dissolved in 3.2 mL of ethanol were added to the reactional medium. pH 2 was reached by

186 adding 0.1 mol L⁻¹ HCl. The resulting gel was kept 24 h at 25 °C and dried at 50 °C without
187 further separation between solid and solvent.

188 In addition, reference samples were prepared in the same conditions without use of
189 spiropyrans and were denominated TEOS-1 (12 mmol TEOS) and TEOS-2 (24 mmol TEOS).

190 3. Characterizations

191 X-ray diffractograms were recorded using the D8 Advance Bruker-AXS diffractometer,
192 with 30 kV, a current of 30 mA and CuK α radiation ($\lambda = 1.5405 \text{ \AA}$). The XRD patterns were
193 obtained between 5-70° (2 θ) with a scan rate of 0.5 degrees min⁻¹. The phase identification was
194 performed using the DIFFRAC.EVA software. To better observe the (001) reflexion, 200 mg
195 of the solids were dispersed in water (2 mL) and were kept under magnetic stirring for 30
196 minutes. Subsequently the mixture was deposited onto a glass slide and dried at 50 °C during
197 24 h and resulted in a film formation. The diffractograms were then collected under the same
198 conditions as for the other samples. ²⁷Al NMR spectra were obtained on a Bruker Avance III
199 spectrometer equipped with a 4 mm H-X MAS probe, operating at a frequency of 130.33 MHz.
200 Calibration was performed using Al(NO₃)₃ (0 ppm) as an external standard.

201 ¹³C CP/MAS NMR spectra were obtained on a Bruker Avance 500 spectrometer
202 operating at a frequency of 60.37 MHz. The proton cross polarization (CP-MAS) was applied
203 with a contact time of 1 ms. The samples were rotated at the magic angle at a frequency of 10
204 kHz. The pulse length of ¹³C was 5 ms (close to $\Pi / 2$) and the recycling delay was 3 s.

205 Thermogravimetric analyzes were performed using a TA Instrument SDT Q600 analyzer,
206 with a heating rate of 10 °C min⁻¹, from 25 °C to 900 °C, under a dry air flow of 10 mL min⁻¹
207 and using an alumina pan.

208

209 3.5 Test of the photoreversibility and UV-Vis diffuse reflectance

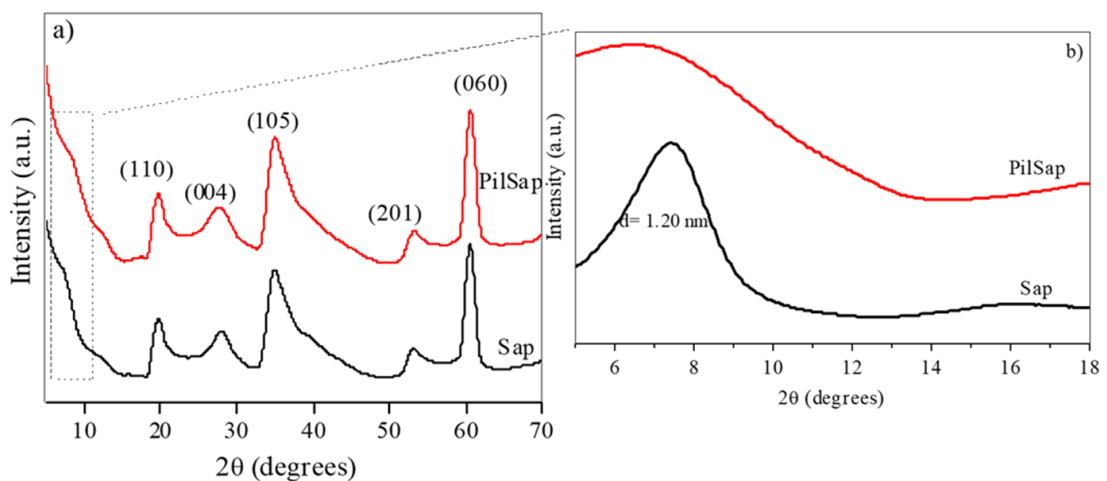
210 Test of the photoreversibility was performed by exposition of the pigments under a white
211 light source for 2 h, using a 66 Klx intensity LED lamp. The pigments were characterized,
212 before and after exposure to light, by diffuse reflectance spectrorimetry performed on an
213 Ocean Optics modular spectrophotometer equipped with halogen and deuterium HL-2000-
214 FHSA light source and incident light beam, with material made from the Ocean Optics
215 USB4000 detector. For each acquisition, 30 scans were accumulated between 400 to 950 nm.

216

217 **4 Results and discussion**

218 4.1 X-Ray diffraction

219 XRD patterns of the raw and pillared saponites are presented in Figure 2. Typical
220 reflections of the saponite were observed at 2θ values of 7.34° associated to a basal spacing of
221 1.21 nm of the saponite and [42] at 60.6° ($d = 0.153$ nm, 060 plan) corresponding to the
222 trioctahedral structure of the clay mineral [43,44]. Other reflections at 2θ of 19.7° , 27.8° , 34.9°
223 and 53.2° were typical of saponite. After pillarization, the (001) reflexion becomes too broad
224 due probably to a heterogeneity in the stacking of the layers. [45–47]. The other reflections of
225 the raw saponite were maintained in the pillared sample.

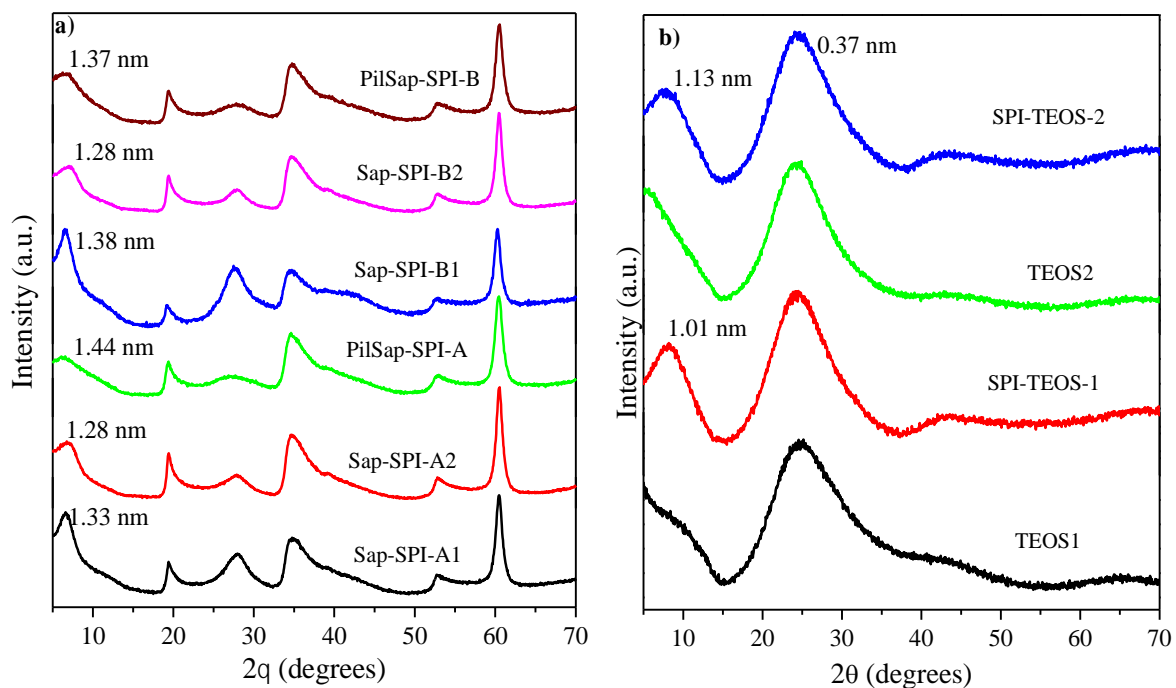


226

227 Figure 2 - X-ray diffractograms of saponite and pillared saponite (a) between 8° and 70° (2θ)
228 and b) between 2° and 18° (2θ).

229 For the pigments prepared with saponite obtained in acidic and basic conditions, the basal
230 spacings were 1.33 nm for Sap-SPI-A1 and 1.38 nm for Sap-SPI-B1 (Figure 3a). However, for
231 the pigments obtained from the pillared saponite, pH influenced the adsorption. Intercalation of
232 the SPI molecule into the interlayer space of the clay mineral, in acidic or basic medium, is not
233 considered since the basal spacing (d_{001}) increased only from 1.37 nm to 1.44 nm in PilSap-
234 SPI-A. In basic medium, phenolate species are present and induce a repulsion between the dye
235 and the external surface of the clay.

236 The XRD results for the pigments obtained by TEOS hydrolysis reactions in acidic
237 medium (Figure 3b) showed broader reflections [48] around 2θ 20-30° characteristics of
238 amorphous silica with a certain degree of organization in the short and medium ranges [49,50].
239 The samples with SPI also presented an amorphous profile with two broad diffraction peaks at
240 2θ equal to 7.82° with spacing values of 1.12 nm and the similar at 2θ of 24.3°.



241

242 Figure 3 - X-ray diffractograms for samples derived from a) saponite and b) TEOS hydrolysis.

243

244 4.3 Solid state NMR

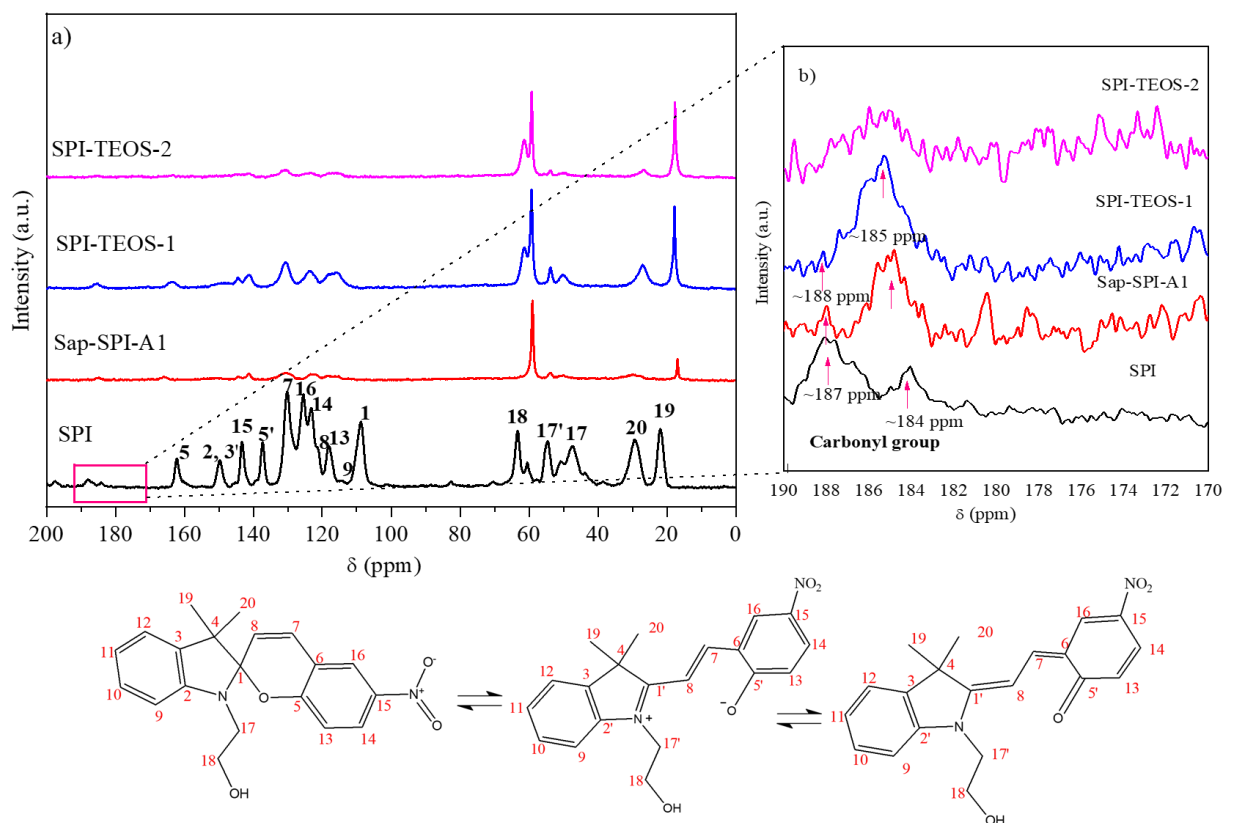
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246 ^{13}C CP/MAS NMR (Figure 5) was useful to confirm the presence of the dye in the
247 pigments and help in the assignment of the interactions between dyes and solids. The SPI
248 spectrum analysis considered the presence of the SP and MC isomeric structures in the dye
249 molecule before and after adsorption and their assignments were based on studies of the free
250 dyes [51,52]. Signals of geminal methyl groups were observed at 21.7 and 29.5 ppm for C19
251 and C20, respectively, furthermore, the lower frequency of C19 in relation to C20 is in
252 agreement with the literature [52]. The signals of the aromatic carbons were in the region of
253 170-100 ppm as well as at 121 and 130 ppm related to unsaturated C8 and C7, respectively
254 [51,52]. Moreover, characteristic signals of carbonyl groups were present in the region between
255 190-170 ppm (Figure 5b), these signals indicate the presence of the carbonylated MC isomeric
256 form and suggest that part of the molecule SPI was in its neutral form. Influence of
257 electronegativity of the atoms that decrease shielding of the carbon was also observed in the
258 NMR spectra [53]. This effect causes shifts in signals, as observed at 162.3 ppm for C5, 149.8
259 ppm for C2 and C3', 143 ppm for C15 and 137.3 ppm for C5'. Other signals were also observed
260 for C1 in 108.7 ppm, C17 in 47.5 ppm, C17' in 54.5 ppm and C18 in 63.3 ppm [52,54,55].

261 For the saponite sample containing spiropyran, the presence of signals related to C18 of
262 the dye shifted from 63.3 ppm in SPI to 59.0 ppm in Sap-SPI-A1. From these results, it is
263 reasonable the interaction between the dye and the saponite through hydrogen bonding between
264 the OH groups of the SPI and the Si-OH, Si-O-Si and Al-OH structural groups of the clay.
265 Similar interactions have been reported for other dyes when adsorbed on smectites [56]. On the
266 other hand, ^{27}Al NMR spectra of the SAP-SPI-A sample did not show any significant changes
267 in the aluminium environment (Figure 6). Thus, it is suggested hydrogen bonding only occurs

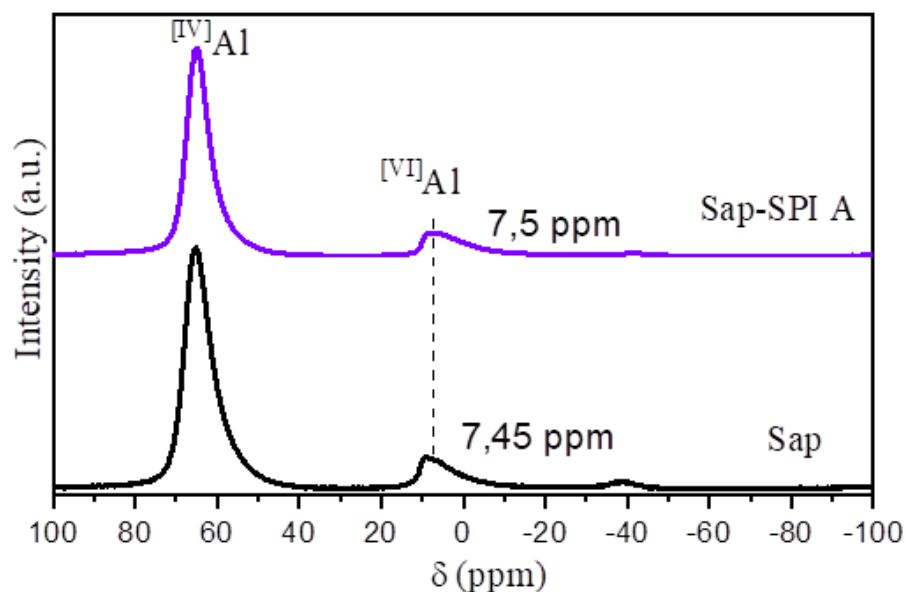
268 between a proton generated hydroxyl group of SPI and silanol groups or oxygen atom in the
 269 saponite surface [72]. The results are in close agreement to the XRD data.

270 For SPI-TEOS samples, ^{13}C CP/MAS NMR spectra presented more defined signals in
 271 the 170 to 100 ppm region, which is characteristic of unsaturated carbons and aromatic ring.
 272 The signals of carbonyl groups were observed between 190-170 ppm for SPI-TEOS-1. In
 273 addition, chemical displacement from 63.0 to 59.0 ppm and from 29.5 to 26.8 ppm were noticed
 274 for signals of the C18 and C20 in SPI, respectively. The observed variations are due to a better
 275 protection of the carbons, suggesting that the interaction of the dye with the polymeric gel also
 276 occurs through hydroxyl groups. Other peaks for the two solids were attributed to the residual
 277 ethoxy groups at 17.8 ppm (O-CH₂-CH₃) and 61.5 ppm (O-CH₂-CH₃) in ethanol [57,58].



278

279 Figure 5 - ^{13}C CP/MAS NMR spectra for SPI and pigments obtained by adsorption ad TEOS
 280 hydrolysis: a) between 200-0 ppm and b) spectra increase between 190-170 ppm.



281

282 Figure 6 - ^{27}Al NMR spectra for precursor matrix and a hybrid pigment obtained by adsorption
 283 of spiropyran in saponite.

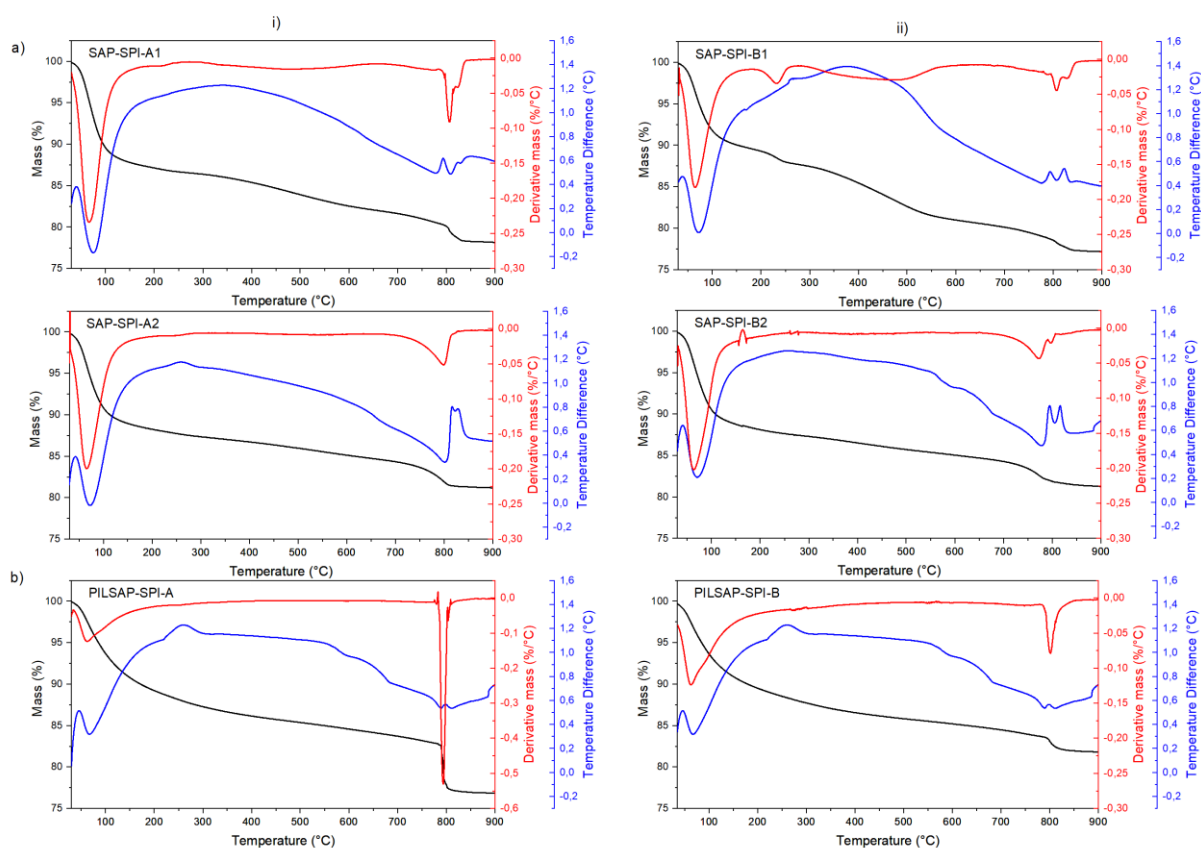
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285 4.4 Thermal analysis

286

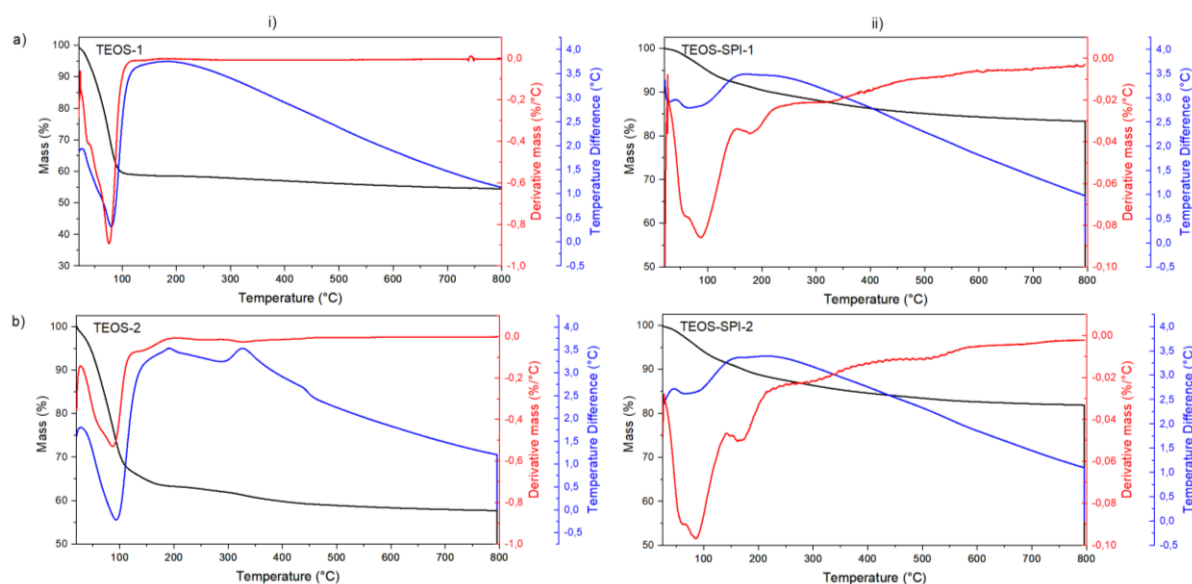
287 The thermal behavior of the prepared samples was investigated using TGA and DTA. All
 288 curves for the prepared pigments are presented in Figure 7-8 and the data are summarized in
 289 Table 2. Raw and pillared saponite presented three stages of mass loss [74]. During initial
 290 heating up to 250-280 °C, both matrices showed endothermic peaks at approximately 65 °C
 291 that corresponded to 9.3% and 5.4% of physisorbed water for Sap and PilSap samples,
 292 respectively. The second event between 250-671 °C is associated to the interlayer water,
 293 reaching the mass losses around 2% for both samples. The third region up to 637-871 °C was
 294 attributed to the dehydroxylation of OH groups which corresponded to 3.4% and 2.9% for raw
 295 and pillared saponite, respectively [59, 74].

296



297

298 Figure 7 – TGA/DTG/TDA curves for the hybrid pigments prepared under i) acid and ii) basic
 299 conditions and based on spirocyan adsorbed onto a) raw saponite and b) pillared saponite.



300

301 Figure 8 – TGA/DTG/DTA curves for i) raw samples and ii) hybrid pigments based on
 302 spirocyan obtained by hydrolysis of a) 12 mmol and b) 24 mmol of TEOS.

303

304 Table 2 - Thermogravimetric data from the raw samples and hybrid pigments based on saponite,
 305 pillared saponite and hydrolysis of TEOS containing a spiropyran dye.

Sample	Event	Temperature (°C)	Mass loss (%)	Total (%)
Sap	I	30-250	9.3	14.9
	II	250-637	2.2	
	III	637-845	3.4	
Sap-SPI-A1	I	30-187	12.6	21.6
	II	187-640	5.1	
	III	661-856	3.9	
Sap-SPI-A2	I	30-219	11.8	18.6
	II	219-673	3.5	
	III	673-852	3.3	
Sap-SPI-B1	I	30-175	10.2	22.7
	II	175-640	9.0	
	III	640-867	3.4	
Sap-SPI-B2	I	30-251	12.2	18.5
	II	251-645	2.9	
	III	645-867	3.4	
PilSap	I	30-280	5.4	8.3
	II	280-671	2.1	
	III	671-871	2.9	
PilSap-SPI-A	I	30-218	11.2	20.1
	II	218-781	6.0	
	III	781-857	2.9	
PilSap-SPI-B	I	30-220	10.9	19.1
	II	220-777	5.4	
	III	777-871	2.9	
TEOS-1	I	30-185	39.0	43.1
	II	185-800	4.1	
TEOS-2	I	30-129	32.2	40.7
	II	129-192	2.9	
	III	192-453	4.1	
	IV	453-800	1.5	
TEOS-SPI-1	I	30-155	7.7	16.4
	II	155-630	7.9	
	III	630-800	0.8	
TEOS-SPI-2	I	30-142	8.2	17.8
	II	142-225	2.4	
	III	225-460	5.2	
	IV	460-800	2.0	

306

307 Sap and PilSap-based pigments also presented three mass loss events (Figure 7). The first
308 step of degradation up to 175-280 °C is assigned to the loss of physisorbed water and
309 dehydration of interlayer cations with a mass loss around 10% for both raw SAP and PilSap-
310 based pigments. Previous studies have shown that free spiropyran dye is stable until 180 °C,
311 being decomposed around 250 °C [51,60]. Thus, the second event up to 640-781 °C is related
312 to both decomposition of organic matter and dehydroxylation [51,60]. After dye loading, the
313 mass losses associated to the second event increased to 5.1%, 3.5%, 9.0%, 2.9%, 2.1%, 6.0%
314 and 5.4% for Sap-SPI-A1, Sap-SPI-A2, Sap-SPI-B1, Sap-SPI-B2, PilSap-SPI-A and PilSap-
315 SPI-B samples, respectively. Lastly, the third event up to 856-871 °C is related to phase
316 transition into enstatite. The results showed that loaded pillared samples did not show major
317 differences in the mass loss associated to the dye (around 3%), once it was applied the same
318 amount of clay matrix in the preparations. However, it is suggested that loaded saponite
319 presented a high dye content in samples with low amount of the clay matrix. The best
320 performance was observed for Sap-SPI-B1 sample, highlighting the loading under basic
321 conditions.

322 For SiO₂ solids obtained from hydrolysis and polymerization of TEOS, two mass loss
323 events were observed for TEOS-1, and four events for TEOS-2 samples (Figure 8). The first
324 event was attributed to the elimination of adsorbed water on the silica surface. The weight loss
325 decreased rapidly to 39% and 32% with endothermic peaks at 110 °C and 123 °C for TEOS-1
326 and TEOS-2, respectively. The second event in TEOS-1 (mass loss of 4.1%) which is probably
327 related to the degradation of the remaining organic matter due to incomplete TEOS hydrolysis
328 and condensation, and to the residual -OH groups on the surface of the silica. [61,62]. It seems
329 that a high amount of TEOS promoted a different polymerization in TEOS-2 samples. Its
330 second stage of decay occurred between 129 °C and 192 °C and can be ascribed to the trapped

331 water molecules between silica particles or into the network structure. The third event (mass
332 loss of 4.1%) is associated to the organic matter from the incomplete hydrolysis of alkoxide
333 TEOS, whereas the last one (mass loss of 1.5%) related to the residual -OH groups on the
334 surface of the silica [61,62]. All mass losses observed for the matrices prepared by hydrolysis
335 of TEOS were accompanied by an endothermic transformation.

336 TGA/DTA curves of pigments based on TEOS showed two stages of mass loss for TEOS-
337 1 and four events for TEOS-2 sample (Figure 8). A decrease in the mass loss related to
338 dehydration on the first stage of both samples (7.7% for TEOS-SPI-1 and 8.2% for TEOS-SPI-
339 2) and an increase of the mass loss in the 2nd and 3rd regions for TEOS-SPI-1 and TEOS-SPI-2
340 samples, respectively, highlighted the load of spiropyran dye with a high content for TEOS-
341 SPI-1 sample. In addition, the dye mass loss occurred from 185-225 °C, simultaneously with
342 the remaining organic matter from the incomplete TEOS hydrolysis.

343

344 4.5 *UV-VIS diffuse reflectance and photochromism test*

345

346 The selected pigments were evaluated by photochromism test and UV-VIS diffuse
347 reflectance spectra were collected before and after the exposure period, as well as in dark
348 condition. Qualitatively, significant color variations were observed for the samples (Figure 9).
349 After test in dark, it was also observed that Sap-SPI-B did not show a color reversibility in the
350 same proportions as occurred for the other samples. This fact probably indicates that in basic
351 medium, the formed pigments have a lower reversibility potential than those formed in acidic
352 medium. On the other hand, the pigments formed by hydrolysis showed more intense colors
353 than the initial solids.



354

355

Figure 9 – Photochromism assay for pigments of spiropyran.

356

357

The UV-VIS diffuse reflectance spectra showed different characteristics for each sample.

358

This fact was related to the color variation of the spiropyran, due to the change in ionization

359

induced by the pH of the medium. The SPI spectrum in Figure 10 presented two bands in the

360

500-600 nm region attributed to the merocyanine (MC) zwitterionic form [7]. Similar spectral

361

profiles have been observed for spiro compounds in nonpolar solutions [67-69]. The planar

362

structure with a prolonged π conjugation between the indoline and chromene portions in the

363

CM, presents a delocalized transition that changes in visible region in relation to closed ring

364

isomer. On the other hand, the spiropyran (SP) form presented two localized transitions at 295

365

nm and 294 nm assigned to the π - π^* electronic transition of the indoline and the chromene

366

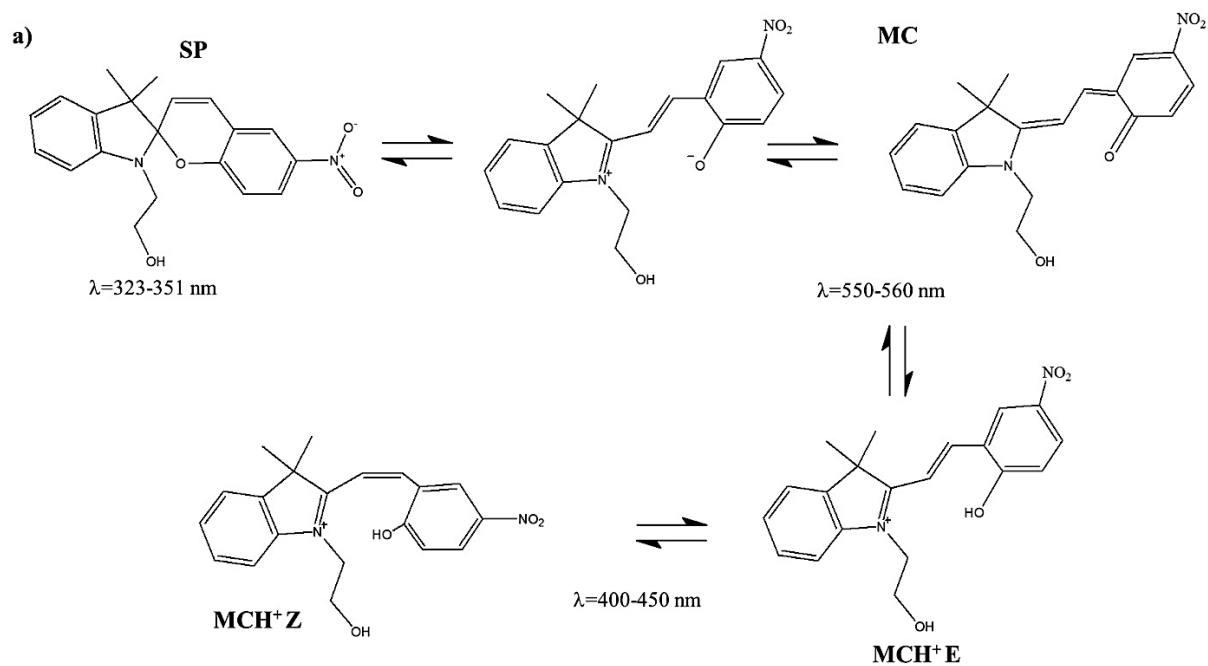
moieties, respectively [67,70,71]. Such understanding allows the differentiation of the isomeric

367

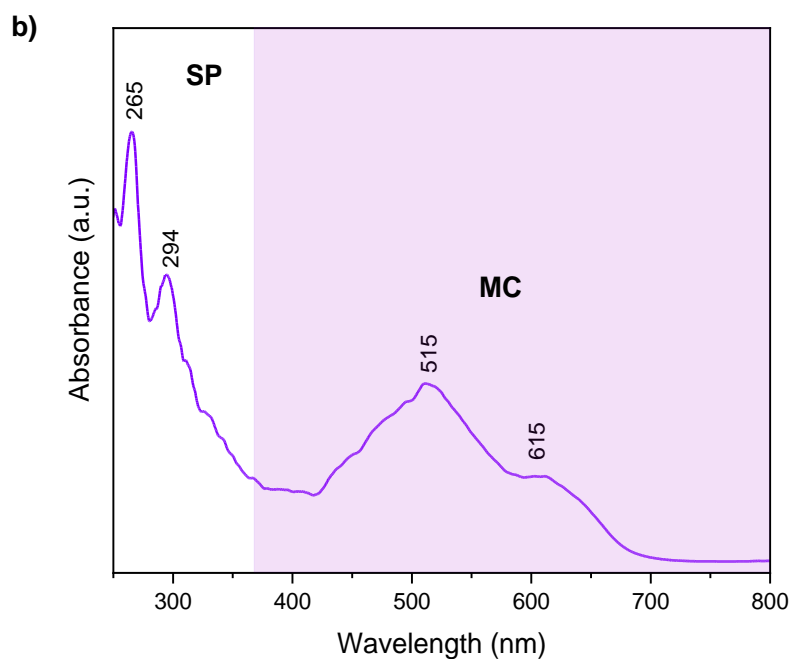
form present in the prepared systems by the analysis of the spectrum and a better understanding

368

of the possible interactions between dye and host matrices.



369



370

371

Figure 10 – SPI H1042 a) isomeric forms and b) UV-Vis absorption spectra.

372

All prepared pigments presented two characteristic absorption bands around 450-550 nm

373

(Figure 11). The first absorption band in the pigments based on saponite and pillared saponite

374

(Figure 11i-iv) at 440 nm was attributed to the MCH⁺ form and the second at 560 nm, observed

375

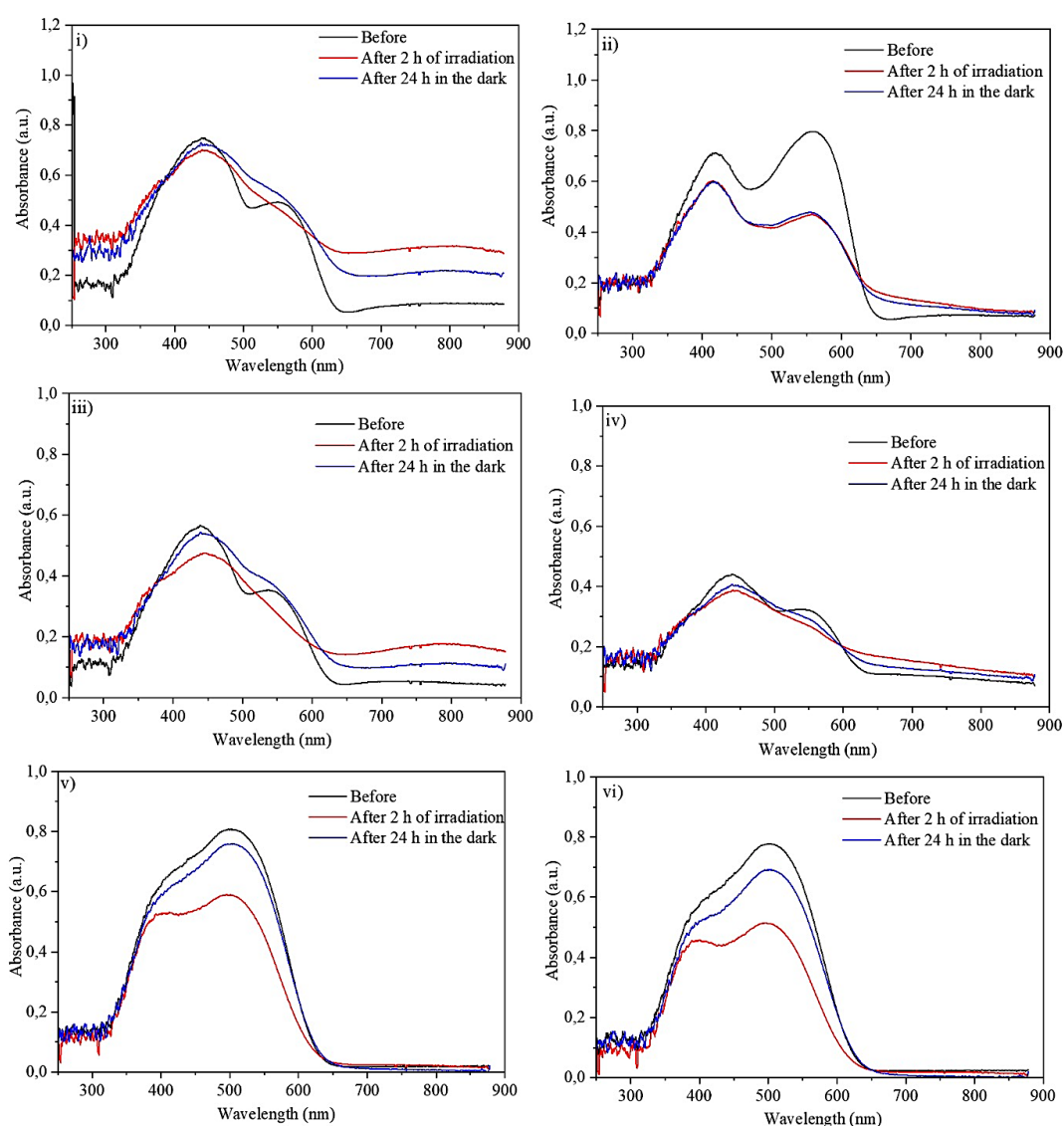
for the four samples may be correlated to the zwitterionic form [55,63]. After reversibility test,

376

the samples obtained in acidic medium presented a broad band centered around 450 nm,

377 suggesting the conversion of the isomeric forms with a predomination of the MCH⁺ form. In
378 contrast, samples prepared under basic conditions have presented minor spectral variations after
379 24 h in the dark.

380 The pigments prepared by TEOS hydrolysis (Figure 11v-vi) exhibited a broad band
381 centered at 500 nm which can be attributed to the predominance of the zwitterionic form [7].
382 Both samples presented some color reversibility, highlighting the effect of the acidic medium
383 for the photoreversible systems.



384

385 Figure 11- UV-Vis spectra for pigments before and after photochromism tests: i) Sap-SPI-A2;

386 ii) Sap-SPI-B2; iii) PilSap-SPI-A; iv) PilSap-SPI-B; v) SPI-TEOS-1 and vi) SPI-TEOS-2.

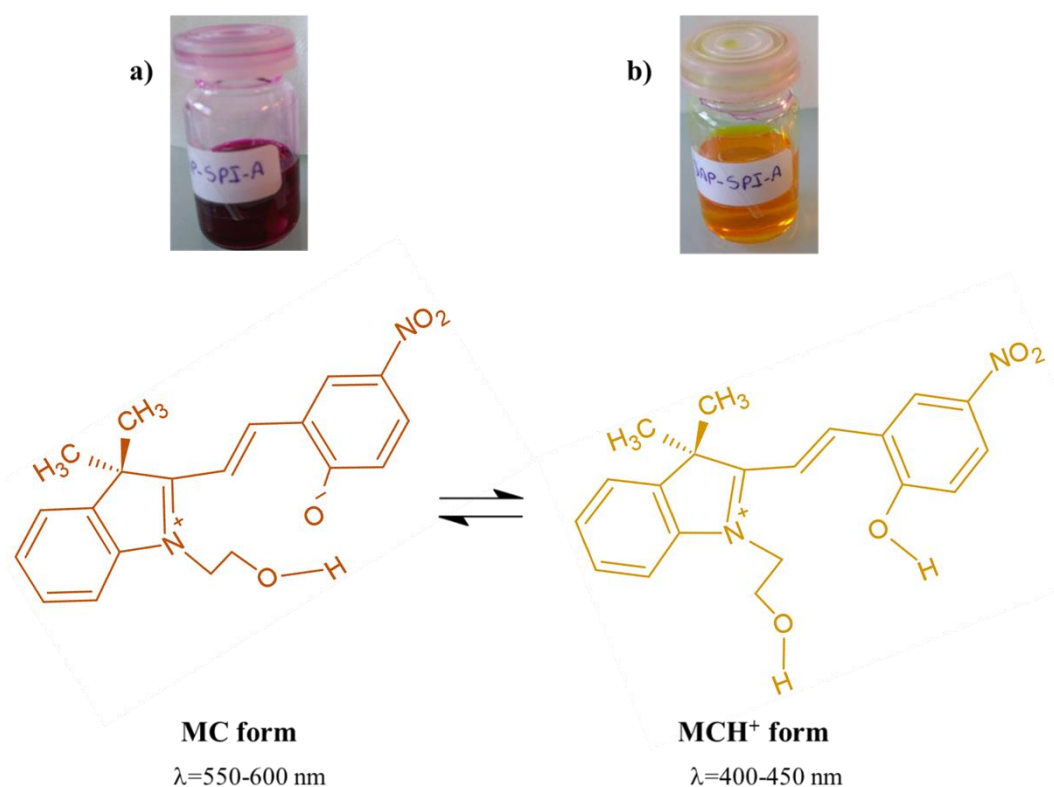
387 All pigments presented a decrease in the bands intensity after light exposure, especially
388 in the region of 400 nm. SPI-TEOS-1 and SPI-TEOS-2 samples. The spectra obtained for the
389 samples after 24 h in the dark presented similar profiles to the initial samples. Except for the
390 Sap-SPI-B2 sample, minor color difference was observed for the samples before and after light
391 exposure. The results suggested the prepared pigments presented photostability with a
392 regeneration capacity after light exposure and subsequent time-out in the dark.

393

394 4.6 *Influence of the pH and isomeric changes*

395 Color variations observed for the prepared hybrid pigments can be explained by the
396 speciation of the SPI dye and the surface charge of the mineral surface which are pH dependent.
397 Regarding clay particles, the literature indicates that their edges are positively charged at pH
398 below 7, although some data suggest they are already neutralized at pH 6 [72]. On the other
399 hand, the surface is negatively charged with the increase of pH values above that. Therefore, it
400 is expected that saponite and pillared saponite exhibited a positive net charge at very low pH
401 such at pH 2, applied in our experiments. Likewise, a negative net charge is expected for these
402 surfaces at very high pH i.e.13, applied in our experiments.

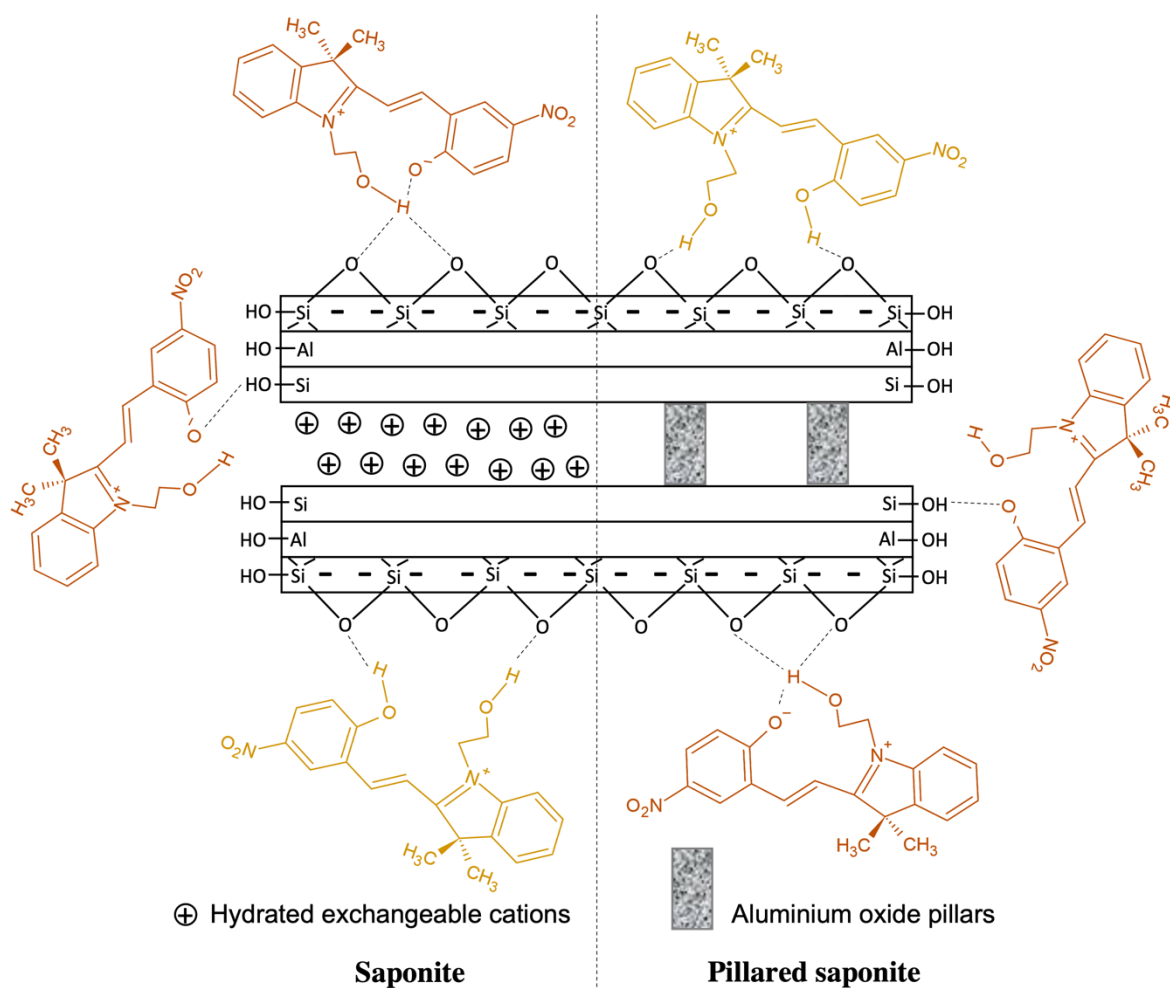
403 In its turn, some spiropyran compounds have chromic acid, and the isomeric variation
404 depends on a favorable medium for the molecular planarization. The polar merocyanine form
405 (MC) is then stabilized in relation to the spiropyran (SP) form when in presence of protons
406 [7,12]. In its zwitterionic form (MC), negatively charged phenolate oxygen can bind to metal
407 cations in an optically controlled reversible process [55]. In addition to complexation with
408 cations, phenolate anion can be protonated, where the molecule shows the MCH^+ form which
409 is detected in the absorption spectrum at 400-450 nm, while the MC isomer at 500-600 nm
410 [7,13,55,63]. The process can also be followed qualitatively, via color variation from purple
411 (MC) to yellow (MCH^+) after protonation, as observed in Figure 12 [64].



413

414 Figure 12 - Illustration of the SPI H1042 isomeric forms a) MC and b) MCH⁺ in acidic solution.

415 UV-Vis data of the prepared pigments have suggested that the MCH⁺ and MC isomeric
 416 SPI forms are stabilized in the proposed silica-based matrices. Based on predicted pK_a = 14.46
 417 \pm 0.10 for H1042 molecule, MC form is partially deprotonated at the pH 13 and is predominant
 418 in experiments under basic conditions. Likewise, MCH⁺ species are dominant in pigments
 419 prepared under acid conditions. From XRD data it is not evidenced intercalation for the saponite
 420 based samples. Moreover ¹³C and ²⁷Al NMR data have suggested that interactions occur
 421 through hydrogen bonding between hydroxyl groups of SPI and silanol groups in the saponite
 422 matrix. In addition, intramolecular hydrogen bonding between proton in hydroxyl groups and
 423 O⁻ generated by cleavage of spirocarbon–oxygen bond is also expected to MC form [73]. Thus,
 424 the following interaction mechanism for the SPI species in the saponite-based pigments is
 425 proposed in Figure 13, considering both MC and MCH⁺ isomeric forms of H1042 spirocyan.



426

427 Figure 13 – Interaction mechanism of the spiropyran species in the saponite-based pigments.

428 Protonated merocyanine interaction with silanol groups of the host matrix through
 429 hydrogen bonds is favored under acid conditions. On the other hand, MC form interacting with
 430 oxygen atoms of the Si-O-Si structural groups of the saponite is dominant under basic
 431 conditions. However, both situations are present in all saponite-based pigments and their color
 432 variations are related to the isomeric forms content adsorbed onto the matrices. In basic
 433 medium, the presence of the phenolate species can generate certain repulsion between the dye
 434 and the layers of the matrix. This effect resulted in less stable pigments than those obtained in
 435 acidic medium. Furthermore, the interaction from silanol groups may promoted steric effects,
 436 impairing intercalation in both pH systems.

437 Analogous to the saponite-based samples prepared under acid conditions, the pigments
438 from the hydrolysis of TEOS presented the predominance of the protonated MC form and the
439 presence of hydrogen bonding as the principal mechanism of dye/silica interaction.

440

441 **5.0 Conclusion**

442

443 Hybrid photochromic pigments were prepared by adsorption of 1'-(2-hidroxietyl)-3',3'-
444 dimetil-6-nitrospiro[1(2H)-benzopirano-2,2'-indoline] on raw and pillared saponites, and by
445 coprecipitation in the presence of hydrolyzed TEOS. The obtained solids were characterized by
446 X-Ray diffraction, ¹³C CP/MAS NMR and thermogravimetry. The color stability of the
447 prepared pigments was evaluated before and after light exposure. Characterization results
448 suggested incorporation of the dye via hydrogen bonding as the principal mechanism of
449 interaction in the pigments. Thermal analysis data indicated that the pigment based on raw
450 saponite with low amount of the clay matrix under basic condition contain a high dye content
451 than those based on pillared saponite under acid condition. The absence of SP bands in the UV-
452 VIS spectra suggested the silica-based matrices stabilized SPI in the MCH⁺ and MC isomeric
453 forms. In addition, the incorporation of the dye in the host silica-based matrices was pH
454 dependent with protonated merocyanine species dominant at pH 2 and zwitterionic
455 merocyanine as major species at pH 13. Regarding the colors, the prepared pigments showed a
456 custom color palette between purple and yellow dependent on the dominant SPI isomeric forms
457 with relative stability after light irradiation. All prepared pigments presented relative
458 photoreversible capacity after recovery at 24 h in the dark. The finds of this study propose the
459 multicolored prepared hybrids as promising materials to be applied in photochromic systems as
460 smart pigments.

461

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