

Stabilization of a hydrophobic natural dye by intercalation into organo-montmorillonite

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1 Stabilization of a hydrophobic natural dye by intercalation into organo-
2 montmorillonite

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18

19 Abstract

20 The stability of the naturally occurring annatto dye against irradiation with visible light
21 was enhanced by intercalation into octyl trimethylammonium and dodecyl
22 trimethylammonium montmorillonite. The intercalated dye exhibited improved light fastness.
23 The effect of the stability enhancement was more distinct with dodecyl trimethylammonium
24 montmorillonite. The reason of the improvement was proved to be the hindrance from the
25 contact with the atmospheric oxygen because the dye molecules were incorporated in the
26 interlayer space. The amount of the adsorbed dye could be increased more than ten times
27 when an aqueous ethanolic solution was used instead of pure ethanol as solvent in the
28 adsorption process.

29

30

31 *Keywords: annatto dye, organo-montmorillonite, surfactant, light fastness, stabilization*

32

1 **1. Introduction**

2

3 Annatto dye is a natural organic pigment belonging to the carotenoids. It is widely used as
4 a food colorant (C. I. Natural Orange 4) because of its low toxicity. The main components of
5 the annatto dye are bixin and norbixin (Scheme 1). The annatto dye is less stable and easily
6 discolored. Light is the most destructive agent (Najar et al., 1988). Therefore, efforts were
7 made to conserve the color of the annatto dye (Prabhakara Rao et al., 2005). Protection of the
8 dye molecule by other materials is one of the approaches. For example, annatto dye was
9 stored in oleoresin to keep its color (Balaswamy et al., 2006) or incorporated in cyclodextrin
10 to improve the stability against light or heat (Lyng et al., 2005).

11 ---Scheme 1---

12 There are some reports concerning the stability enhancement of the dye by the
13 incorporation into the interlayer space of clay minerals (Bauer et al., 2003; Bujdák et al.,
14 2002; Chakraborty et al., 2011; Giustetto et al., 2011). We recently studied the stability
15 enhancement of natural dyes by intercalating them into the interlayer space of several clay
16 minerals. Anthocyanin, a cationic natural dye, was intercalated into montmorillonite (Kohno
17 et al., 2009a). The color stability in alkaline medium or against visible light was drastically

18 improved by the intercalation. On the other hand, the anionic dye carmine was intercalated
19 into hydrotalcite, and the light fastness of the dye was enhanced. However, the annatto dye
20 could not be intercalated into the polar interlayer space of the hydrotalcite (Kohno et al.,
21 2009b). Bixin and norbixin can be considered as anionic dyes because they have carboxyl
22 group(s). However, the long conjugated double bond chain in their structure makes the
23 annatto dye strongly hydrophobic. Therefore, to incorporate the annatto dye between the clay
24 mineral layers, the interlayer space must be hydrophobized.

25 Organo-clay minerals were reported to have the ability to incorporate various organic
26 compounds (Lagaly et al., 2006) such as dyes (Sasai et al., 2004; Sasai et al., 2003; Tong et
27 al., 2010), pesticides (Cruz-Guzman et al., 2005; Groisman et al., 2004) or herbicides (Celis et
28 al., 2007; Seki and Yurdakoç, 2005). We succeeded in the intercalation of non-ionic
29 (hydrophobic) 2-hydroxychalcone derivatives into organo-montmorillonite and the
30 photochemical conversion of the chalcone to the flavylum form (Kohno et al., 2011). In this
31 study, we report the intercalation of the hydrophobic natural annatto dye into
32 organo-montmorillonite to enhance its light stability.

33

34 **2. Experimental**

35

36 *2.1 Sample preparation*

37

38 The annatto dye (ANA) was supplied by Wako Chemical Co. and used without further
39 purification. Montmorillonite Kunipia F (denoted as KF) was supplied by Kunimine Industry.
40 The cation exchange capacity (CEC) of KF was 1.19 meq/g. Octyl trimethylammonium
41 bromide (OTAB) and dodecyl trimethylammonium bromide (DTAB) were obtained from
42 Tokyo Chemical Industry and used as received.

43 To modify KF with the surfactants, 0.2 g of KF were mixed with 2 cm³ of an aqueous
44 solution containing 0.46 mmol of the surfactant. After stirring for 2 h and standing for 24 h,
45 the organo-montmorillonites (denoted as O-KF and D-KF) were separated by filtration and
46 dried on air.

47 The adsorption of ANA on O-KF and D-KF was carried out as follows. First, 10 mg of
48 ANA were dissolved in 10 cm³ of ethanol. The ethanol solution of ANA was mixed with 0.2
49 g of O-KF or D-KF, and the dispersion was permitted to stand for 24 h in the dark. The
50 amount of the dye corresponded to 5 mass% of O-KF or D-KF. The sediment was collected
51 by filtration, dried at room temperature and ground to powder. The filtrates remained colored,

52 indicating that not all ANA molecules were adsorbed.

53 A mixture of water and ethanol (1:4 v/v) was also used instead of pure ethanol. The
54 amount of the introduced dye was controlled by changing the volume of the added dye
55 solution. A required volume of the ethanolic solution of ANA (1 mg/cm^3) was mixed with
56 20% (v/v) of water. The aqueous ethanolic solution of ANA was then mixed with 0.2 g of
57 D-KF and maintained for 24 h in the dark. The solids were obtained by filtration and drying at
58 room temperature. These samples are denoted as $\text{ANA}_{\text{w-}x}/\text{D-KF}$, where x represents the
59 amount of the dye added to the sample (x mass% of D-KF) and ranged from 5 to 20 %.
60 Except for $\text{ANA}_{\text{w-}20}/\text{D-KF}$, the filtrates of the samples were colorless, indicating that all of the
61 ANA molecules were adsorbed onto D-KF.

62 Silica was used as the reference adsorbent. The silica was supplied from Catalysis Society
63 of Japan (JRC-SIO-6, designated as SIO). SIO (0.2 g) was dispersed in 10 cm^3 of an ANA
64 ethanolic solution containing 10 mg of ANA. The amount of ANA added was 5 % of silica.
65 The ethanol was evaporated under an air stream in the dark at room temperature.

66

67 *2.2 Measurements*

68

69 XRD patterns were measured with the Rigaku MiniFlex X-ray diffractometer (CuK α , step
70 angle and scan speed 0.05° and 2°/min, 15mA, 30 kV). UV-Vis spectra were collected with
71 the JASCO V-550 spectrophotometer. For the measurement of diffuse-reflectance spectra, the
72 ISV-469 integrating sphere was equipped to the spectrometer. To investigate the light
73 endurance of each sample, the samples were irradiated with visible light under ambient
74 temperature and pressure. A 100 W halogen lamp (Schott Megalight 100) equipped with a 30
75 cm length flexible light guide was used as the visible light source. The powder samples were
76 loaded in a plastic cell covered with a thin glass and placed 1.1 cm from the aperture of the
77 light guide. The degree of the color fading was determined by the decrease of the absorption
78 of ANA measured by the diffuse reflectance spectra. When the sample was irradiated in the
79 absence of oxygen, the sample cell was packed in a transparent gas barrier film filled with
80 nitrogen.

81

82 **3. Results and discussion**

83

84 *3.1 Structural analysis*

85

86 The XRD patterns of KF, O-KF and D-KF samples are illustrated in Fig. 1. The reflection
87 of KF at around $2\theta = 7.4^\circ$ was assigned to the 001 reflection. The 001 reflection of O-KF and
88 D-KF shifted to lower angle, indicating the increase of the basal spacing of O-KF and D-KF
89 compared with the original KF. Considering the thickness of the silicate layer of KF as 0.96
90 nm, the interlayer distance of O-KF and D-KF was calculated to be 0.43 nm and 0.83 nm,
91 respectively. These values were in good agreement with the reported value (Klapyta et al.,
92 2001; Ogawa and Kuroda, 1997; Ogawa et al., 1992). Since the interlayer distance of O-KF
93 (0.43 nm) corresponded to the size of the polar head group of the surfactant molecule, it was
94 suggested that OTAB molecules formed a monolayer between the layers of KF. The interlayer
95 distance of D-KF of 0.83 nm indicated bilayers of the surfactant ions in the interlayer space
96 (Ogawa and Kuroda, 1997; Ogawa et al., 1992). The formation of the bilayers of DTAB
97 makes the interlayer space more hydrophobic.

98 ---Figure 1---

99 The dye was not adsorbed on KF itself, so that ANA/KF was not colored and the XRD
100 patterns of KF and ANA/KF were identical. The XRD patterns of ANA/O-KF and
101 ANA/D-KF were almost the same as those of O-KF and D-KF, respectively. Thus, the
102 layered structure of the organo-montmorillonite was maintained after the adsorption of the

103 dye. Since the interlayer distance was not changed by the adsorption of the dye, the ANA
104 molecules were probably dissolved in the *pseudo*-organic phase formed by the surfactant ions
105 between the clay mineral layers.

106

107 *3.2 UV-vis spectra*

108

109 The diffuse-reflectance UV-Vis spectra normalized at the wavelength of maximal
110 absorption are represented in Fig. 2. The solution of ANA exhibited absorption peaks at 455
111 nm and 482 nm together with a shoulder at 427 nm. ANA/SIO showed a single broad
112 absorption band with λ_{max} at 430 nm. The fine structure observed in the spectrum of the ANA
113 solution was lost, and the main peak shifted to shorter wavelength in ANA/SIO. These results
114 suggested the aggregation of the adsorbed dye molecules. ANA/O-KF and ANA/D-KF
115 exhibited a couple of peaks at 460, 490 nm and 462, 492 nm, respectively, with a shoulder
116 band at around 435 nm. The spectral shape of ANA/O-KF and ANA/D-KF resembled that of
117 the ANA solution suggesting that the ANA molecules were not aggregated but dispersed in
118 ANA/O-KF and ANA/D-KF as in the solution. Compared with the spectrum of the dye
119 molecules in the solution, the peaks were shifted by 5 to 10 nm to longer wavelengths. The

120 reason of the red shift in ANA/O-KF and ANA/D-KF was not sufficiently clarified yet. The
121 spectral shift mechanism of carotenoids caused by the medium is still under investigation by
122 several research groups, and the dispersion, polarization or interaction between charges was
123 proposed (Renge and Sild, 2011; Yanagi et al., 2006). However, at least we can say that the
124 ANA molecules were in an environment different from the solution. This suggests that the
125 ANA molecules were surrounded by the alkyl chains of the surfactant ions between the clay
126 mineral layers.

127 ---Figure 2---

128

129 *3.3 Light fastness*

130

131 The spectral changes during irradiation are shown in Fig. 3. In every sample, the
132 absorption of ANA decreased and the color was faded by the irradiation. The shape of each
133 spectrum did not change drastically during the fading process, indicating that the process was
134 not a photochemical conversion but a simple photo-degradation of the dye.

135 ---Figure 3---

136 The time course of the absorption of the adsorbed ANA during irradiation is illustrated in

137 Fig. 4. Serious photo-fading was observed on ANA/SIO, and only 11% of the dye remained
138 after 60 min irradiation. The light fastness of ANA/O-KF was not very good (24%). The most
139 stable sample was ANA/D-KF showing considerable endurance against irradiation (55%).

140 ---Figure 4---

141

142 *3.4 Cause of the stability enhancement*

143

144 To evaluate the effect of the atmospheric oxygen on the light fastness, ANA/D-KF and
145 ANA/SIO were subjected to irradiation under nitrogen (Table 1). After 60 min irradiation,
146 ANA/D-KF maintained 55% and 79% of the absorption of ANA under atmosphere and
147 nitrogen, respectively. Thus, the light fastness of ANA/D-KF was slightly improved under
148 nitrogen. While the retention of ANA absorption of ANA/SIO was only 11% in the air, the
149 value was remarkably improved to 71% under nitrogen. Since ANA molecules are susceptible
150 to oxidative degradation, the stabilization effect observed under nitrogen is interpreted as a
151 hindrance from the contact of atmospheric oxygen. Therefore, we concluded that the ANA
152 molecules in ANA/D-KF were protected from oxygen by the alkyl groups of the surfactant
153 ions in the interlayer space. Although an organic phase generally tend to dissolve more

154 oxygen molecules, inhibition of the direct contact with gaseous oxygen significantly
155 enhanced the stability of the incorporated dye.

156 ---Table 1---

157 The stability of ANA/O-KF against irradiation was less than that of ANA/D-KF because
158 the dye molecules in the interlayer space were less protected by the shorter alkyl chains. The
159 monolayer arrangement of the octyl trimethylammonium ions in the interlayer space might be
160 another reason (see section 3.1). Ogawa *et al.* also reported that anthracene or naphthalene
161 was not clearly intercalated into montmorillonite modified by octyl trimethylammonium ions
162 (Ogawa et al., 1992).

163

164 *3.5 Improvement in the dye adsorption*

165

166 The color of ANA/D-KF was not strong because the amount of adsorbed ANA was not
167 large. For the utilization as a colorant, the sample should exhibit a deeper color. Therefore, we
168 tried to increase the amount of adsorbed dye by changing the solvent used in the dye
169 adsorption procedure. Table 2 represents the absorbance of ANA adsorbed on D-KF from
170 aqueous ethanolic solutions. The absorbance of the dye roughly corresponded to the amount

171 of the adsorbed dye. The addition of water considerably increased the amount of dye adsorbed.
172 ANA_{w-5}/D-KF and ANA_{w-10}/D-KF adsorbed almost all ANA added since the filtrate was
173 colorless. The absorbance of ANA_{w-5}/D-KF reached a 7 times higher value compared to
174 ANA/D-KF. Since the ANA molecules preferred a hydrophobic environment, the increase in
175 the polarity of the solvent pushed the ANA molecules toward the hydrophobized clay mineral
176 layers.

177 ---Table 2---

178 The absorbance of ANA_{w-10}/D-KF was nearly twice that of ANA_{w-5}/D-KF (Table 2).
179 However, the absorbance of ANA_{w-20}/D-KF was almost the same as that of ANA_{w-10}/D-KF. In
180 fact, on preparing ANA_{w-20}/D-KF, the filtrate remained colored, indicating that part of the
181 added dye was not adsorbed. Therefore, the adsorption of ANA on D-KF was almost
182 saturated in ANA_{w-10}/D-KF.

183 The light fastness of the ANA_{w-x}/D-KF series (Table 3) was not so different.
184 ANA_{w-5}/D-KF and ANA_{w-10}/D-KF exhibited a little improved photostability compared with
185 ANA/D-KF. This suggests that the ANA molecules were more deeply incorporated in the
186 clay mineral interlayer because of the more polar solvent used in the adsorption process. The
187 photostability of ANA in ANA_{w-20}/D-KF was lower than those of ANA_{w-5}/D-KF and

188 ANA_{w-10}/D-KF. Perhaps, the excess ANA molecules in ANA_{w-20}/D-KF were adsorbed on the
189 external surfaces of the clay mineral particles, and such dye molecules were easily discolored
190 by the oxidation under irradiation.

191 ---Table 3---

192

193 **4. Conclusion**

194

195 As a hydrophobic natural dye, annatto dye was intercalated into montmorillonite if the
196 interlayer space was hydrophobized by alkyl trimethylammonium ions. The annatto
197 dye/organo-montmorillonites showed higher photostability than the pure annatto dye because
198 the dye molecules were protected from the external oxygen by the layered structure of
199 montmorillonite. Modification with dodecyl trimethylammonium ions was superior to octyl
200 trimethylammonium ions in the improvement of the photostability of the annatto dye.
201 Probably, the dodecyl trimethylammonium ions presented a more suitable environment for
202 the adsorption of the dye. The amount of dye adsorbed was increased by using aqueous
203 ethanolic solutions instead of pure ethanol in the adsorption process. The light fastness was
204 not considerably influenced by the amount of the dye. The stabilized annatto dye is expected

205 to be widely used as an environmentally friendly colorant.

206

207 **Acknowledgment**

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211

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278

279 Figure captions

280

281

282 **Figure 1.** XRD patterns of (a) KF, (b) O-KF and (c) D-KF.

283

284 **Figure 2.** (a) UV-Vis spectrum of the ethanolic solution of ANA and diffuse reflectance UV-Vis spectra of (b)

285 ANA/SIO, (c) ANA/O-KF and (d) ANA/D-KF.

286

287 **Figure 3.** Changes in the absorption spectra of (a) ANA/SIO, (b) ANA/O-KF and (c) ANA/D-KF during visible

288 light irradiation of 60 min.

289

290 **Figure 4.** Absorption of ANA-montmorillonites at λ_{\max} during irradiation of 60 min. (a) ANA/SIO, (b)

291 ANA/O-KF and (c) ANA/D-KF. The ordinate is the ratio of the absorbance to the initial value.

292

Tables

Table 1. Light fastness of ANA/SIO and ANA/D-KF in the presence or absence of oxygen.

	ANA/D-KF	ANA/SIO
A/A_0 in the air ^a	0.55	0.11
A/A_0 under N ₂ ^a	0.79	0.71

^a Ratio of the absorption at λ_{\max} before and after irradiation of 60 min.

Table 2. Changes in the absorbance of ANA by the solvent used in the adsorption step.

Sample	ANA/D-KF	ANA _{w-5} /D-KF	ANA _{w-10} /D-KF	ANA _{w-20} /D-KF
A_{460} ^a	0.08	0.54	1.01	1.12
$A_{460}/A_{460(\text{ANA/D-KF})}$ ^b	1	7	13	14

^a Absorbance at λ_{\max} (460 nm).

^b Ratio of the absorbance of each sample to that of ANA/D-KF at λ_{\max} , reflecting the increase in the amount of adsorbed ANA.

Table 3. Light fastness of ANA/D-KF with various amounts of ANA loading.

Sample	ANA/D-KF	ANA _{w-5} /D-KF	ANA _{w-10} /D-KF	ANA _{w-20} /D-KF
A/A_0 ^a	0.55	0.65	0.67	0.57

^a Ratio of the absorption at λ_{\max} before and after irradiation of 60 min.

Scheme 1

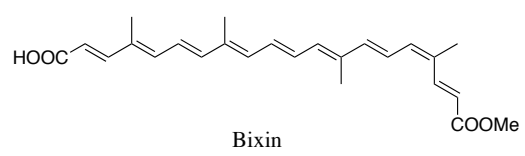
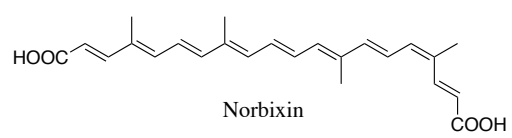


Figure 1

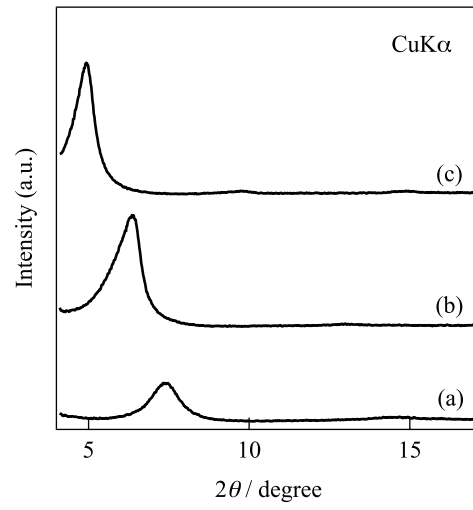


Figure 2

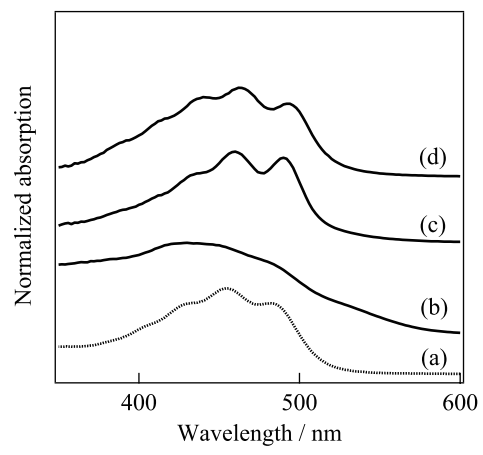


Figure 3

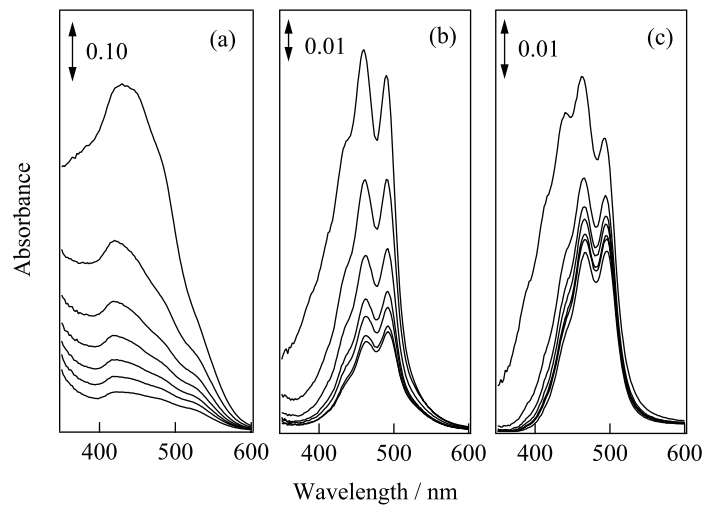


Figure 4

