Photostability enhancement of Methyl orange by intercalation into hydrotalcite, and its dyeing on cotton

Yusmaniar
1 Dept of Chemistry State Univercity of Jakarta

Abstract: The aim of this study is the improvement of the photostability of anionic dye, methyl orange (MO), by intercalation into the hydrotalcite layer (Mg-F-MO LDH). It was found that the thermostability of MO was markedly improved by intercalation into the hydrotalcite host, whilst the photostability was enhanced slightly. The effect of the stability enhancement is larger when the amount of introduced MO exceeds 0.21 g/g-host, or when the layer charge density of the hydrotalcite is larger. Infrared spectroscopy and thermogravimetric analysis revealed the presence of hostguest interactions between hydrotalcite layers and MO anions. With an isothermal heating at 100°C and 150°C for 2 h, the material exhibited a colour retention of approximately 95%. Mg-Fe-MO LDH were found to have much higher colour strength than that obtained in MO. The application of MO and Mg-Fe-MO LDH for dyeing cotton fabric by exhaust method. It was found that washing fastness, rubbing fastness and light fastness produced with Mg-Fe-MO LDH have better colour strength than the MO.

Keywords: MO, Mg-Fe-MO LDH, dyeing, cotton

I. INTRODUCTION

Layered double hydroxides also known as hydrotalcite-like compounds or anionic clays, have received much attention in the past decades due to their wide spread applicability. LDH have positively charged layers of metal hydroxides and the anions and water molecules are located between the layers. The positive charges that are produce from the isomorphous substitution of divalent cations and trivalent cations, are counter balanced by anions located between the layers[1]. LDHs have a general formula of \([\text{M}^{2+}_{x} \cdot \text{M}^{3+}_{\text{x}}, \text{A}^{-}_{\text{y}}, \text{nH}_{2}\text{O}]\). Where M\(^{2+}\) and M\(^{3+}\) are divalent and trivalent metal cations, respectively, A is the anions, and x is ratio \(\text{M}^{2+} + \text{M}^{3+} \neq x\). The anions between the layers can be polymers, organic dyes, surfactants and organic acids [3].

This type of material can be synthesised directly by co-precipitation or the so-called spontaneous self-assembly method [4], in which the host and the guest species are included in the mother liquor, followed by aging process to form a well-ordered layered nanocomposite. Alternatively, the host has to be prepared first, followed by modification or further treatment of the host and finally insertion of the guest molecule inside the interlayers [5,6]. Attempts have been made to intercalate various dye molecules, in particular organic dyes inside layered inorganic lamella, especially anionic clays for various purposes and applications. For example, work on the formation of nanocomposite layered inorganic LDH containing intercalated dye was done by several researchers. The dye used included naphthol blue black [7], indigo carmine and cocaine [8] and water soluble dye which is useful for ink jet technology [9].

In the present study, intercalation of an anionic dye, methyl orange into the Mg–Fe-CO\(_3\) LDH to form an organic–inorganic nanohybrid composite material and the subsequent effects on the structure and the morphology by X-ray diffraction (XRD), and infrared spectroscopy (FTIR) were studied.

II. EXPERIMENTAL WORK

A. Synthesis of Mg-Fe-CO\(_3\) LDH

A mixed solution of MgCl\(_2\) \(\cdot\)6H\(_2\)O (from 0.2 to 0.5 mol) and 0.1 mol of FeCl\(_3\) \(\cdot\)6H\(_2\)O in 100 ml of distilled water was added drop wise under vigorous stirring to 100 ml of an aqueous solution containing 0.2 mol of Na\(_2\)CO\(_3\) and 0.1 mol of NaOH. During the co-precipitation process, the pH was maintained at a constant value equal to 10 by addition of 3M NaOH solution. The suspension was stirred during 24 h at 80°C for maturation and then centrifuged. The obtained material was washed with distilled water until obtaining a Cl- free LDH (AgNO\(_3\) test),
dried during 24 h at 105°C, ground in an agate mortar and 250 m sieved. A fraction of the obtained material was calcined at 500 °C during 8 h. The obtained solid was designated as Mg-Fe-CO₃ LDH.

B. Synthesis of Mg-Fe-MO LDH

Methyl orange (MO) intercalated LDH (MgFe-MO LDH) was synthesized by an anion-exchange method using Mg-Fe-CO₃ LDH as precursor, similar to that already reported [28]. The intercalation was typically carried out as follows: A portion of the filter cake (9.2 g, containing ca. 7.3 mmol CO₃⁺) was dispersed in 100 mL water under N₂ protection to form a white slurry and a solution of methyl orange (20 g, molar ratio of methyl orange to CO₃⁺) in 300 mL water was added to the slurry under a nitrogen atmosphere. The concentration of methyl orange in the final solution was about 0.097 M and the pH value was adjusted to 4.6 by adding 0.01 M HNO₃. The reaction was carried out under a nitrogen atmosphere at 100°C for 96 h after the mixture was microwave treated for 1 h. The resulting precipitate was centrifuged at a speed of 4200 revolutions per minute and thoroughly washed with water and then further washed with DMF until the supernatant was nearly colorless. Finally, the product was washed twice with 100 mL ethanol and then dried at 100°C for 24 h.

C. Characterization of the Mg-Fe-MO LDH

Powder X-ray diffraction data were collected with monochromatic Cu K radiation (λ = 1.540589 Å). FT-IR spectra of LDH and Mg-Fe-MO LDH (KBr disc samples) were recorded on a NICOLET Avatar 330 FT-IR spectrophotometer in the region of 400–4000 cm⁻¹.

D. Thermo- and photostability of MO and Mg-Fe-MO LDH

MO/PE and Mg-Fe-MO LDH/PE were separately incorporated into a polyethylene resin (PE) with the content of MO in the composite being 0.5 wt.% in each case. The MO/PE and Mg-Fe-MO LDH /PE composite sheets of size 50 x 50 x 1 mm were molded and thermally aged in an oven at 100, 150 and 200°C for 30 min. The color difference (ΔE) value was recorded after each heating step (A ΔE reading of 0 represents a perfect match and a value of 1 is supposed to represent the smallest variance the human eye can see, although the sensitivity of the human eye is not uniform across the visible spectrum).

The MO/PE and Mg-Fe-MOLDH/PE composite sheets were photoaged in a UV photoaging instrument (with an ultraviolet high pressure mercury lamp as UV light source, 1000 W power and wavelength range 250-380 nm) with a temperature control system. The color difference (ΔE) value was recorded after UV irradiation for 5 min. The process was repeated ten times, giving a total of 50 min accumulated exposure for each composite sheet.

E. Dyeing cotton fabrics

Cotton fabrics (1 g) were pretreated with 5 g/l of nonionic detergent, at 60°C for 20 min prior to being used for the dyeing. The samples were dyed in a dyeing apparatus using acetic acid (pH 4-5) and L: R = 40:1. The build up properties of Mg-Fe-MO LDH on cotton fabrics were obtained by dying with dye solutions 0.1%, 0.5%, 1%, 2% and 4% owf (Ohio Works First). Dyeing was carried out by raising the dye bath temperature from 30 to 100°C at the rate of 2°C/min, holding at this temperature for 45 min and cooling down at 70°C at the rate of 3°C/min (Fig. 2).
III. RESULTS AND DISCUSSION

A. Characterization

1. XRD analysis of the samples

The powder X-ray diffraction pattern of LDH with Mg/Fe molar ratios shows peaks at 7.7 Å (d0 0 3), 3.84 Å (d0 0 6), 2.64Å (d0 1 2), 1.55Å (d1 1 0) and 1.52Å (d1 1 3), which is similar to those reported by several authors [10]. By analyzing the X-ray diffractograms we obtained that cell parameters are a = 3.10 Å and c = 23.1 Å for LDH sample which are in good agreement with previous reports [11]. The influence of Mg/Fe molar ratios was apparent, it can be see from XRD (Fig. 1a) that with Mg/Fe molar ratio equals 3, the good cristalinity and higher hydrotalcite content in sample were obtained.

The diffractogram pattern of CLDH (hydrotalcite calcined) (Fig. 1) shows peaks at 2θ = 43.06° and 62.48° which are corresponding to MgO, and at 2θ = 30.2°, 35.5°, 43.06°, 57.2° and 62.5° which can be attributed to the MgFe₂O₄ (magnesioferrite) spinel structure (JCPDS 17-0465) those peaks have been observed by Ferreira et al. [10] and Zhang et al. [12].

2. FTIR analysis of the samples

Fig. 2 displays the FTIR spectra of MgFeCO₃LDH, in the 4000-400 cm⁻¹ wave number range. are typical of layer double hydroxides and agree well with the typical results obtained by Ferreira et al. [26]. The broad band
observed at 3400-3500 cm\(^{-1}\) is attributed to the interlayer water molecules, this band become weaker and is shifted at 3411 cm\(^{-1}\) when hydrotalcite is calcined. The weak band at 1647 cm\(^{-1}\) is due to the bending vibration (deformation mode of HOH (H–O–H)) of interlayer water molecules in LDH [11]. The strong band at 1359 cm\(^{-1}\) is due to the mode 3 of the interlayer carbonate species as reported in the literature [26,30]. The bands in the range of 582 and 663 cm\(^{-1}\) are attributed to Mg-O and Fe-O stretching.

3. UV Visible Spectra

Fig. 3 demonstrates the diffuse reflectance UV visible spectra of powdered samples of MO and Mg-Fe-MOLDH after heated in an oven at 100, 150, 200, 250, and 300\(^{\circ}\)C for 30 min. The absorption spectrum of MO shows significant changes on heating at temperatures above 150\(^{\circ}\)C, especially in the range from 400 to 800 nm. With increasing temperature, the changes in the spectra become much more marked. This indicates that MO begins to decompose at 150\(^{\circ}\)C and it is further decomposed as the temperature is increased above 150\(^{\circ}\)C. In the case of Mg-Fe-MO LDH, however, there is no significant change in the spectra after heating below 250\(^{\circ}\)C. Even after heating at 300\(^{\circ}\)C, the spectrum changes only slightly in the range from 700 to 800 nm, suggesting that Mg-Fe-MO LDH can tolerate higher temperatures than MO. These results conclusively demonstrate that the thermostability of the MO is enhanced after intercalation into the interlayer galleries of the Mg-Fe-LDH.

![Figure 3](image)

**Fig. 3.** UV visible spectra of MO (a) and Mg-Fe-MO LDH (b) after thermal aging at different temperatures.

B. Photostability of Mg-Fe-MO LDH

Powdered samples of MO and Mg-Fe-MO-LDH were photoaged in a UV photoaging instrument equipped with a temperature control system. The color difference (\(\Delta E\)) values of the irradiated samples (Fig. 4) were measured using the CIE 1976 \(L^*a^*b^*\) method every 5 min up to a total exposure time of 50 min. The \(\Delta E\) values for MO are considerably larger than those for Mg-Fe-MO LDH after irradiation for the same times. The \(\Delta E\) value of MO exceeds 2.9 after aging for 50 min, whereas the DE value for Mg-Fe-MO LDH is less than 1.1. These values suggest that the photostability of MO anions is improved by intercalation into the interlayer galleries of Mg-Fe-MO LDH. This is possibly due to the presence of the strongly hydrogen bonded network in the interlayer galleries between the hydroxyl groups of the layers and the MO.
C. Comparison of shades of natural MO and Mg-Fe-MO LDH

The shade and tone could also be evaluated by viewing the L*, a*, b*, C* and h values. Value L*, a*, b*, C* and h for MO and Mg-fe-MO LDH is given in Table 1. L* represents lightness value, the higher the lightness value represent lower the colour yield. a* and b* Represent the tone of the colour, positive values of a* and b* represent redder and yellower tones while negative shows greener and bluer tones. C* represents chroma or purity of colour. h Represent hue (shade) of colour. The comparison of shades and tones of Mg-Fe-MO LDH with MO through their colour coordinate values is also given in Table 1. These values demonstrate the matching of MO shade and tone with Mg-Fe-MO LDH.

<table>
<thead>
<tr>
<th>Dye type</th>
<th>Colour coordinates</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>L*</td>
<td>A*</td>
<td>B*</td>
<td>C*</td>
<td>h</td>
</tr>
<tr>
<td>MO</td>
<td>46.72</td>
<td>5.21</td>
<td>27.36</td>
<td>27.46</td>
<td>77.83</td>
</tr>
<tr>
<td>Mg-Fe-MO LDH</td>
<td>49.95</td>
<td>8.36</td>
<td>28.89</td>
<td>30.45</td>
<td>73.12</td>
</tr>
</tbody>
</table>

D. Comparison of fastness properties of MO with Mg-Fe-MO LDH

1. Washing fastness

The wash fastness of fabric dyed for MO and sample dyed Mg-Fe-MO LDH are indicated in Table 2. These results were assessed in the usual way in terms of the grey scale values for the staining of adjacent cotton material and alteration in shade. It is indicated that sample with natural dye extract and mordanted with iron Mg-Fe-MO LDH gave rating good to very good washing fastness in comparison to the very good to excellent rating for shade developed with Mg-Fe-MO LDH. The very good to excellent washing fastness of sample dyed with Mg-Fe-MO LDH was due to the strong covalent bonds between the reactive dye molecules and the cotton fabric. But it can be seen that sample dyed with MO is also comparable to sample dyed with Mg-Fe-MO LDH.

2. Light fastness

Light fastness values of cotton fabric dyed with MO and Mg-Fe-MO LDH are indicated in Table 2. The results for Mg-Fe-MO LDH were good to better according to grey scale rating. The higher light fastness properties of Mg-Fe-MO LDH can be attributed to the strong intramolecular H-bonding which exists in the form of six membered rings. This enhances the stability of the compound by a reduction in electron density at the chromophore. As a result sensitivity of dye towards photochemical oxidation becomes reduced.
3. Rubbing fastness

Table 4 shows the rubbing fastness of sample dyed with MO and dyed with Mg-Fe-MO LDH. It was observed that both types of dyes showed almost similar behavior towards rubbing fastness. This observation can be correlated to the fact that both types of dyes are equally penetrated into the cotton fabric.

<table>
<thead>
<tr>
<th>Dye type</th>
<th>Colour coordinates</th>
<th>MO</th>
<th>Rubbing fastness</th>
<th>Light fastness</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Wash fastness</td>
<td>Rubbing fastness</td>
<td>Light fastness</td>
<td></td>
</tr>
<tr>
<td>Alt</td>
<td>Sc</td>
<td>Dry</td>
<td>Wet</td>
<td></td>
</tr>
<tr>
<td>MO</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Mg-Fe-MO LDH</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>6</td>
</tr>
</tbody>
</table>

IV. CONCLUSION

MO and Mg-Fe-MO LDH and were separately incorporated in a polyethylene (PE) resin with the content of MO in the composite being 0.5 wt.%. It should be pointed out that the color of MO began to change during the preparation of the MO/PE composite, suggesting MO started to decompose during the course of incorporation. However, there was no color change in the case of Mg-Fe-MO LDH. MO/PE composite sheets were heated in an oven at 100, 150 and 200°C for 30 min and the ΔE values were recorded after each treatment. The ΔE values for MO/PE, are larger than those for Mg-Fe-MO LDH/PE after thermal aging at the same temperatures, suggesting that the Mg-Fe-MO LDH/PE composite has better thermostability than the MO/PE composite.

V. ACKNOWLEDGMENT

The support of this research by Ministry of Education of Indonesia under Hibah Bersaing grant.

REFERENCES