



An easy and effective method for the intercalation of hydrophobic natural dye into organo-montmorillonite for improved photostability

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ABSTRACT

β -carotene (BC) is one of the naturally occurring dyes belonging to the carotenoids group. Although it is more environmentally friendly and better suited for humans compared with synthetic dyes, it destabilizes with light and heat, easily losing its color under irradiation. Extended application of BC are therefore limited. The aim of this study is to improve the stability of BC by intercalation into the montmorillonite layers modified with a cationic surfactant, by a simple mixing and minimal solvent use. The physical mixing of small quantities of concentrated BC/hexane solutions with organo-modified montmorillonite successfully resulted in the composite material. The length and the number of alkyl chains of the surfactant used for the organic modification influenced the stability enhancement of the incorporated dye. The improved stability of the dye molecules incorporated in the interlayer space was found to be due to restricted contact with atmospheric oxygen.

1. Introduction

Naturally occurring dyes are more environmentally friendly and suitable for humans, compared with their synthetic counterparts. These dyes find extensive use in cosmetics and food industries. β -carotene (BC) is one such dye, a well-known constituent of the carotenoid group dyes. The structure of the BC is shown in Scheme 1. BC shows strong hydrophobic and lipophilic properties due to its long unsaturated carbon chain, as well as the hydrocarbon groups not containing oxygen at both ends of the chain [1]. From a human health viewpoint, BC is known to be an antioxidant, protecting cells against reactive oxygen species and free radicals [2–4]. Unfortunately, natural dyes such as BC are generally quite reactive and easily lose their color by light or heat [5,6]. Extensive practical application of BC as colorants are therefore substantially hampered. If the stability of BC could be improved, its broadened use as a safe and environmentally friendly coloring material could be realized [7, 8].

Incorporation of natural and synthetic dyes into inorganic host materials is known as a promising method to improve the stability. For instance, the incorporation of dyes into clays [9–11], zeolites [12–15], and mesoporous silicates [16,17] has been reported to enhance the

stability of the guest dye molecules. In a previous report, the dye perylene-3,4,9,10-tetracarboxylic diimide was intercalated into layered double hydroxide and montmorillonite. The intercalated dye was shown to have improved photostability [18,19]. We have also investigated the improved stability of various natural dyes by producing dye composites with nontoxic inorganic host materials [20–22], including montmorillonite [23]. Montmorillonite is a clay mineral with a layered structure composed of an octahedral Al_2O_3 or MgO sheet between two tetrahedral SiO_2 sheets. There are exchangeable cations between the layers of montmorillonite to compensate for the net negative charge of the octahedral sheets [24,25]. In a previous study, we proved that the cationic anthocyanin dye could be successfully intercalated and stabilized in the interlayer space of the montmorillonite [23]. Such clays were, however, found to be incapable of intercalating carotenoid dyes because they are generally hydrophobic and nonionic [26].

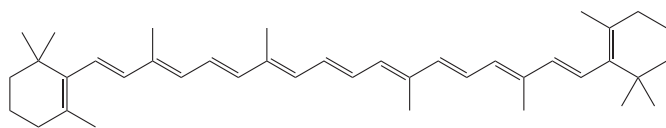
Modifying the interlayer space of the clays, including montmorillonite, with cationic surfactants such as alkyl ammonium ions via an ion exchange reaction can transform the hydrophilic interlayer space into a hydrophobic one [27–30]. The surfactant-modified montmorillonite is named organo-montmorillonite and is known to exhibit different adsorption properties compared with the original clay mineral [31,32].

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Scheme 1. Molecular structure of β -carotene.

Based on this technique, BC has been reported to be successfully intercalated in the interlayer space of the organo-montmorillonite [33]. The intercalation of a hydrophobic carotenoid dye (annatto dye) into organo-montmorillonite, exhibiting improved its stability, has also been achieved by our group [34].

Organic solvents have been used to prepare the composites thus far. This is due to the notion that the dye molecules had to be fully dispersed in the organic solution in order to be more easily adsorbed onto the host materials. This method requires solvent waste treatment facilities and composite drying processes at elevated temperature, both of which are practically disadvantageous and environmentally unfriendly. In a previous report, it was found that BC could be successfully incorporated into the pores of the organo-modified mesoporous silicates by solventless physical mixing due to the hydrophobic interaction. This resulted in the stabilization of BC [22]. It has also been reported that carotenoids can be successfully intercalated into arabinogalactan by a mechano-chemical method, rendering aqueous solubility [35]. It can therefore be expected, similar to the organo-modified mesoporous silicates and arabinogalactan, that the hydrophobic interaction could also promote the intercalation of BC between the layers of the organo-modified clay by the simple physical mixing, just like other organic compounds reported earlier [36].

In this study, we sought to prepare BC/organo-montmorillonite composite with limited solvent use. Two methods were used to achieve this end. The first is through solventless physical mixing, where the powdery organo-montmorillonite and BC are mixed together directly. The second method is through the mixing of powdery organo-montmorillonite and a small amount of a concentrated BC/hexane solution. Because the amount of the hexane solution used is minimal and the solvent can be easily evaporated during mixing, this procedure was named the “semi-dry mixing method”. These methods could eliminate solvent waste and additional drying processes, resulting in a reduction of cost and energy consumption. The efficiency of the semi-dry mixing

method for the preparation of intercalated composites was first evaluated. The enhanced stability of BC in the composite with organo-montmorillonite prepared by the semi-dry mixing method was then investigated. The influence of the length and number of alkyl chains of the surfactant on the stability of the incorporated BC was also of interest. This was done to evaluate the effect that the intercalation had on the stability of the composite. Through these methods, we were able to investigate whether the semi-dry mixing method was effective for the intercalation of BC into organo-montmorillonite.

2. Experimental

2.1. Sample preparation

BC was supplied by Wako Chemical Co. As the montmorillonite, Kunipia F (denoted as KF) was supplied by Kunimine Industries. The cation exchange capacity (CEC) of KF was 115 meq/100 g. Dodecyltrimethylammonium bromide (DTAB) and hexadecyltrimethylammonium bromide (HTAB) were purchased from Wako Chemicals. Octyltrimethylammonium bromide (OTAB), dioctyltrimethylammonium bromide (DODAB), didodecyltrimethylammonium bromide (DDDAB), and dihexadecyltrimethylammonium bromide (DHDAB) were purchased from Tokyo Chemical Industry. Silica was supplied by the Catalysis Society of Japan (JRC-SIO-6, denoted as SIO) and was used as the reference adsorbent.

To modify KF with the OTAB, DTAB, and HTAB, KF (2 g) was mixed with an aqueous solution containing the surfactant (100 cm^3 , 4.6 mmol), which corresponded to a CEC of 200%. The mixture was stirred at room temperature for 6 h and was then left to stand for 24 h. The sediments were then separated by filtration and dried under vacuum for 6 h at 323 K. The obtained organo-modified KF were denoted as C8KF, C12KF and C16KF, respectively. To modify KF with the DODAB, DDDAB, and DHDAB, KF (2 g) was mixed with an aqueous solution containing the surfactant (400 cm^3 , 2.3 mmol), which corresponded to a CEC of 100%. The mixture was stirred for 6 h at 343 K and was then left to stand for 24 h, after which the sediments were separated by filtration. After filtration, excess surfactant on the sediments was removed by washing out with water, and the sediments were dried under vacuum for 6 h at 323 K. The obtained organo-modified KF were denoted 2C8KF, 2C12KF, and 2C16KF, respectively.

The adsorption of BC on the organo-modified KF by the semi-dry mixing method was performed as detailed. First, a BC/hexane solution (1 cm^3) containing BC (0.2 mg) was mixed with the organo-modified KF (0.2 g). The mixture was then sealed in a glass vial bottle ($\phi = 1.8\text{ cm}$, volume = 5 cm^3) with the addition of 10 particles of a zirconia ball ($r = 1.80\text{--}2.00\text{ mm}$). The vial was then horizontally rotated at 300 rpm for 1 h in the dark. Although the obtained samples were near-dry, they were left in air at room temperature for 1 h in the dark, to ensure complete dryness. These samples were denoted BC/C8KF, etc. The preparation method of BC/SIO included physically mixing BC/hexane solution (1 cm^3) containing BC (0.2 mg) with SIO (0.2 g) and the zirconia ball for 1 h, similar to the preparation of BC/C8KF and the related composites.

The solventless physical mixing method was conducted separately, in order to determine the effect that the added hexane had on the preparation of the composites. In this preparation method, the BC powder (0.2 mg) and 2C16KF (0.2 g) were physically mixed in a mortar for 10 min. This sample was denoted BC/2C16KF-dry.

2.2. Measurements

XRD patterns were collected using a with Rigaku MiniFlex X-ray diffractometer ($\text{CuK}\alpha$, step angle and scan speed $0.50^\circ/\text{min}$, 15 mA, 30 kV).

UV-Vis spectra were collected using a JASCO V-550 spectrophotometer. For the measurement of diffuse-reflectance spectra, an ISV-469 integrating sphere was coupled to the spectrometer.

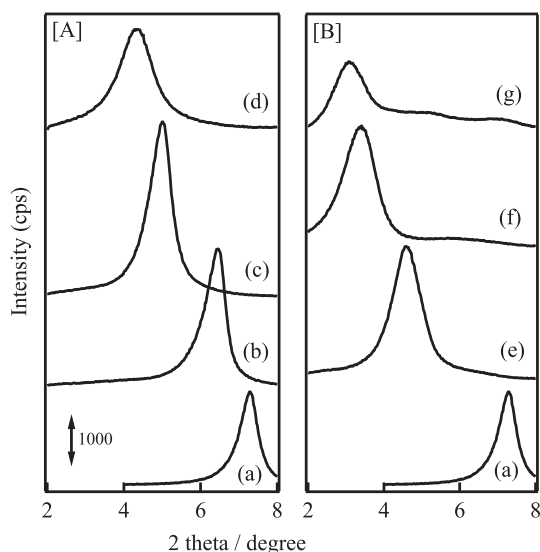


Fig. 1. XRD patterns of (a) KF, (b) C8KF, (c) C12KF, (d) C16KF, (e) 2C8KF, (f) 2C12KF, (g) 2C16KF. Panel [A] indicates the XRD patterns of KF modified with the surfactant having single alkyl chains, whereas panel [B] indicates those having double alkyl chains.

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